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ESTIMATED CONTAMINANT LOADINGS IN THE ST. CLAIR AND DETROIT RIVERS - 1984

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ESTIMATED CONTAMINANT LOADINGS

IN THE

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Great Lakes Section
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FOREWORD

This report discusses concentrations and estimated loadings of trace contaminants in the Lake Huron/Erie corridor during 1984. An assessment of this type, involving identification of significant sources, sinks and loss mechanisms can provide an understanding of the fate and transport of contaminants in the system. In addition, the potential for impact on subsequent downstream water bodies may be more clearly understood.

Comprehensive work presently being conducted as part of the binational (Canada/U.S.) Upper Great Lakes Connecting Channels Study (UGLCCS) will provide a more detailed database upon which to improve estimates of loadings.

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1.0 SUMMARY OF FINDINGS

A 1984 investigation conducted by the Great Lakes Section of the Water Resources Branch revealed an increase in estimated loadings within the St. Clair - Detroit River system. Significant increases were evident in the Sarnia "Chemical Valley" and downstream of the Windsor/Detroit corridor, where peak concentrations were measured.

Elevated levels of hexachlorobenzene (HCB) at Sarnia and of octachlorostyrene (OCS) further downstream confirmed earlier observations of high levels and inputs associated with the eastern (Ontario) shore of the St. Clair River. Polychlorinated biphenyl (PCB) inputs from Michigan sources in the upper Detroit River were responsible for very high levels monitored along the entire western shore of the Detroit River. A step-wise increase in concentrations of heavy metals (iron, lead, and zinc) was generally observed in the system with increasing distance downstream. Significant inputs of these compounds were noted downstream of the Detroit vicinity along the Michigan shoreline. Peak mercury concentrations were observed at the mouth of each river.

Quantification of specific organic compounds in whole water was not possible, as most were below the routine method detection limits for whole water analysis. However, measured values were obtained for HCB, OCS and PCBs on centrifuged particulates. Estimation of whole water concentrations from particulates and organic carbon-corrected partition coefficients enabled spatial trends to be identified.

Lateral variability in measured concentrations was accounted for by employing flow-weighted loading estimates. Contaminants were mainly confined to the eastern nearshore of the St. Clair River and the western nearshore of the Detroit River, and as such, flow-weighted contaminant levels were used to predict loads. Variability in flow rates of river segments was attributed to wind and storm events causing enhancement or reduction, depending upon wind direction and speed. Minimal flow enhancement occurred through lateral (e.g. tributary) inputs.

Relative changes in loadings between river segments identified Lake St. Clair as a potential sink for contaminants, largely through settling of contaminated particulates. Lake St. Clair also has a significant potential for losses of organics through a number of degradation pathways, as well as volatilization to the atmosphere. Loadings were observed to decrease for several parameters in the lower Detroit River, likely the result of settling of particulates from reduced velocity or dilution from increased lateral distribution; however, trends were not as discernable as in Lake St. Clair. It should be noted that loading calculations are estimates based on a number of assumptions, and can be considered suitable only for relative comparisons or trends.

1.0 RÉSUMÉ DES RÉSULTATS

L'enquête effectuée en 1984 par la Section des Grands Lacs de la Direction des ressources en eau a révélé une augmentation des concentrations de produits polluants dans les eaux des rivières St. Clair et Détroit. Cette augmentation a été particulièrement nette dans la "Zone de la chimie" des environs de Sarnia et en aval du couloir Windsor-Détroit, où ont été enregistrées les concentrations les plus fortes.

Les concentrations d'hexachlorobenzène (HCB) et d'octachlorostyrène (OCS) enregistrées respectivement à Sarnia et en aval ont confirmé les résultats antérieurs concernant la concentration et le volume des produits déversés sur la rive est (Ontario) de la rivière St. Clair. Les biphényles polychlorés (BPC) déversés au Michigan dans la partie supérieure de la rivière Détroit expliquent les très fortes concentrations enregistrées tout le long de la rive occidentale de la rivière Détroit. On a généralement constaté une augmentation progressive des concentrations de métaux lourds (fer, plomb et zinc) à mesure qu'on descendait les rivières. Des quantités importantes de ces composés sont déversées en aval de Détroit le long de la rive du lac Michigan. De très fortes concentrations de mercure ont été relevées à l'embouchure des deux cours d'eau.

Il n'a pas été possible de calculer les quantités exactes des divers composés organiques présents dans l'eau non filtrée parce que, pour la plupart, leur concentration était inférieure à celles que permet de détecter la méthode courante d'analyse de l'eau non filtrée. Par contre, on a pu mesurer les concentrations de HCB, d'OCS et de BPC sur des particules centrifugées. On a estimé les concentrations de polluants dans l'eau en analysant

les particules et en appliquant des coefficients de partage pondérés par le taux de carbone organique, ce qui a permis de dégager des tendances spatiales.

Pour tenir compte de la variabilité latérale des résultats obtenus, on leur a appliqué un facteur de pondération en fonction du courant. Les plus fortes concentrations étaient situées près de la rive orientale de la rivière St. Clair et près de la rive occidentale de la rivière Détroit; c'est pourquoi on a appliqué le facteur en question pour calculer les charges. La variabilité du débit d'un point des rivières à l'autre dépendait du vent et des orages; on notait une augmentation ou une réduction en fonction de la direction et de la vitesse du vent. On constate une augmentation minime du débit aux endroits où se produit un apport d'eau latéral (soit au débouché des affluents).

Les différences de concentration enregistrées à divers points de rivière indiquent que le lac St. Clair risque de se transformer en réservoir de matières polluantes, principalement à cause du dépôt de particules contaminées. Le lac St. Clair présente aussi un risque sensible de perte de matières organiques par diverses voies de décomposition ainsi que par volatilisation dans l'atmosphère. La concentration de plusieurs produits tend à diminuer dans le cours inférieur de la rivière Détroit, probablement parce que les particules se déposent, le courant étant moins rapide, ou parce que la dilution augmente à mesure que la rivière s'élargit. Cependant, ces tendances ne sont pas aussi visibles que dans le lac St. Clair. Il faut préciser que les charges ont été estimées à partir d'un certain nombre d'hypothèses et qu'elles ne peuvent servir qu'à faire des comparaisons ou à dégager des tendances.

2.0 INTRODUCTION

Inputs of persistent trace contaminants to the St. Clair and Detroit River system are a cause of concern, resulting in "significant environmental degradation and severe impairment of beneficial water uses" (International Joint Commission, 1983).

This "system" may be subdivided into three compartments: (i) The St. Clair River, receiving its flow from relatively pristine Lake Huron and contaminant inputs primarily from the Sarnia "Chemical Valley"; (ii) Lake St. Clair, which may act on contaminants through a number of physical, chemical and biological processes; and (iii) the Detroit River, which receives throughput from the above two compartments, and contaminants from the heavily industrialized Detroit/Windsor corridor.

3.0 OBJECTIVES

As a preliminary investigation, this study was intended to convey an overview of trace contaminant concentrations in the St. Clair and Detroit Rivers and provide gross loading estimates. Identification and quantification of contaminants at points entering and exiting each river system was used to map the degree and extent of impairment and identify major 'sources' and 'sinks.' Relative differences in loadings between river compartments allow an assessment of the origin and fate of contaminants. Areas which appear to be contaminant 'sinks' will be identified, with discussion of possible mechanisms which act on contaminants. Other aspects such as lateral distribution and additional factors which may impact on loading estimates will also be discussed.

4.0 METHODS

Four surveys were conducted along the extent of the St. Clair and Detroit Rivers from May to November, 1984. Figure 1 illustrates sampling locations and provides an overview of the Lake Huron/Erie corridor. Stations were situated at both the head and mouth of the St. Clair and Detroit Rivers as well as midpoint in the latter. Stations SR39-100 and SR39-1500 were located at the head of the St. Clair River, 62 km (39 mi) from the river's mouth and 30 m (100 ft) and 457 m (1500 ft), respectively, from the U.S. shore. Sample locations CE17, SR10S and SR10N located at the St. Clair River mouth were situated at approximately the midpoint of the Chenal Ecarte, South Channel and the North Channel, respectively. Samples were also obtained in the vicinity of the Sarnia "Chemical Valley" during the last survey at stations located between transects SR33.1 and SR34.98 (see Figure 2).

Stations DT30.8W and DT30.7E were located at the head of the Detroit River adjacent to U.S. and Canadian shores, respectively (Figure 3). Stations DT17.4W and DT17.0E were situated immediately downstream of the large urban-industrial complexes of Detroit and River Rouge, Michigan and Windsor, Ontario respectively. Sample locations at DT9.3 were located along a transect 792m (2600 ft), 1219 m (4000 ft) and 1524 m (5000 ft), from the U.S. (Grosse Isle) shore and 15 km (9.3 mi) from the river mouth. Station DT8.7 W was located at midpoint in the Trenton Channel 14 km (8.7 mi) from the river's mouth.

Sampling occurred during four discrete periods from: May 16 to June 2; June 5 to June 17; August 2 to August 26 and October 30 to November 22. During each period, individual (single) samples were obtained from all locations, with the exception of stations DT17.4W and DT17.0E, at which duplicate samples were taken. Temperature, dissolved oxygen and pH profiles were measured at 2-metre-depth increments at each station prior to sampling.

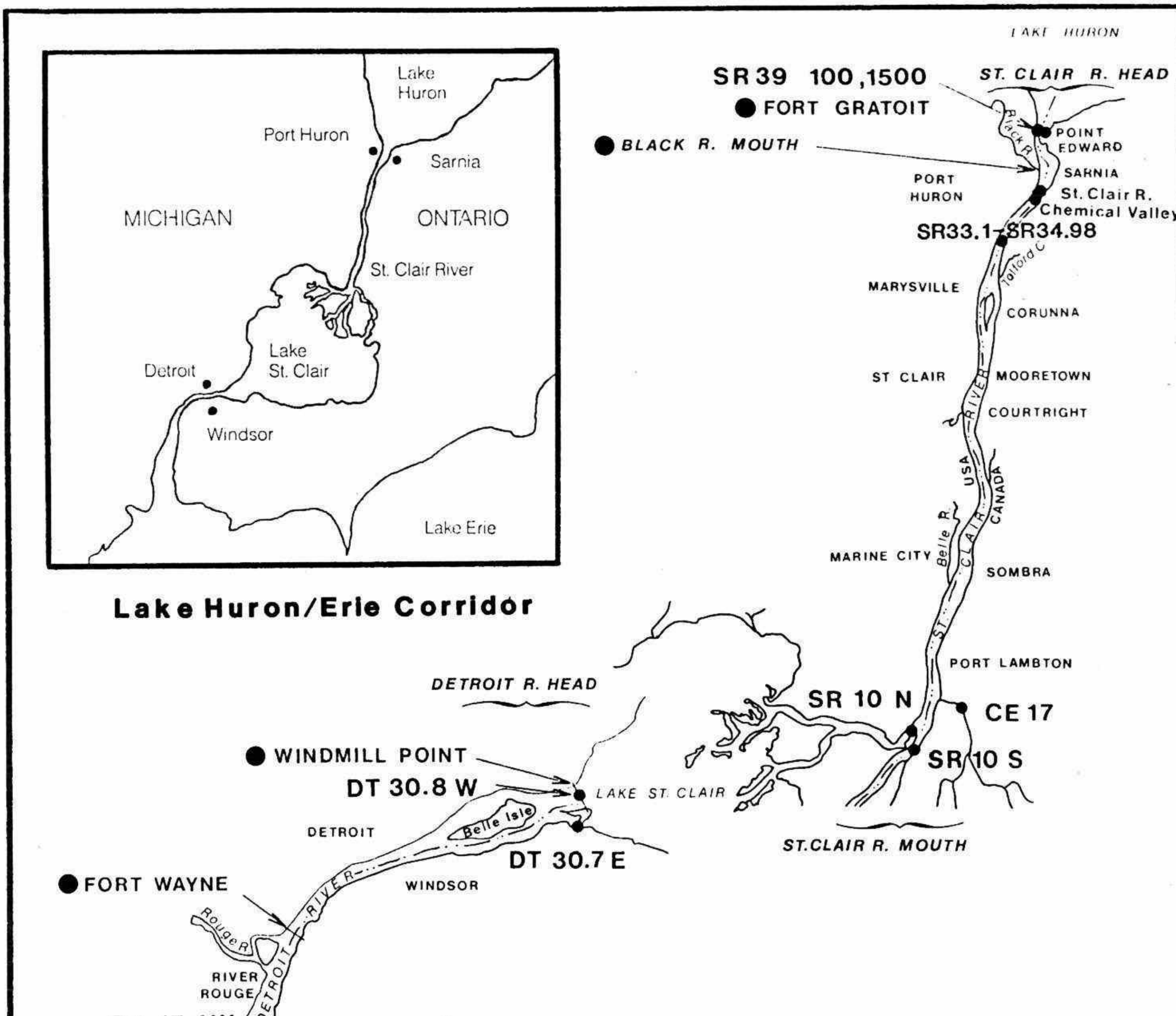

FIGURE 1: St. Clair/Detroit Rivers - Overview of study area and sampling locations

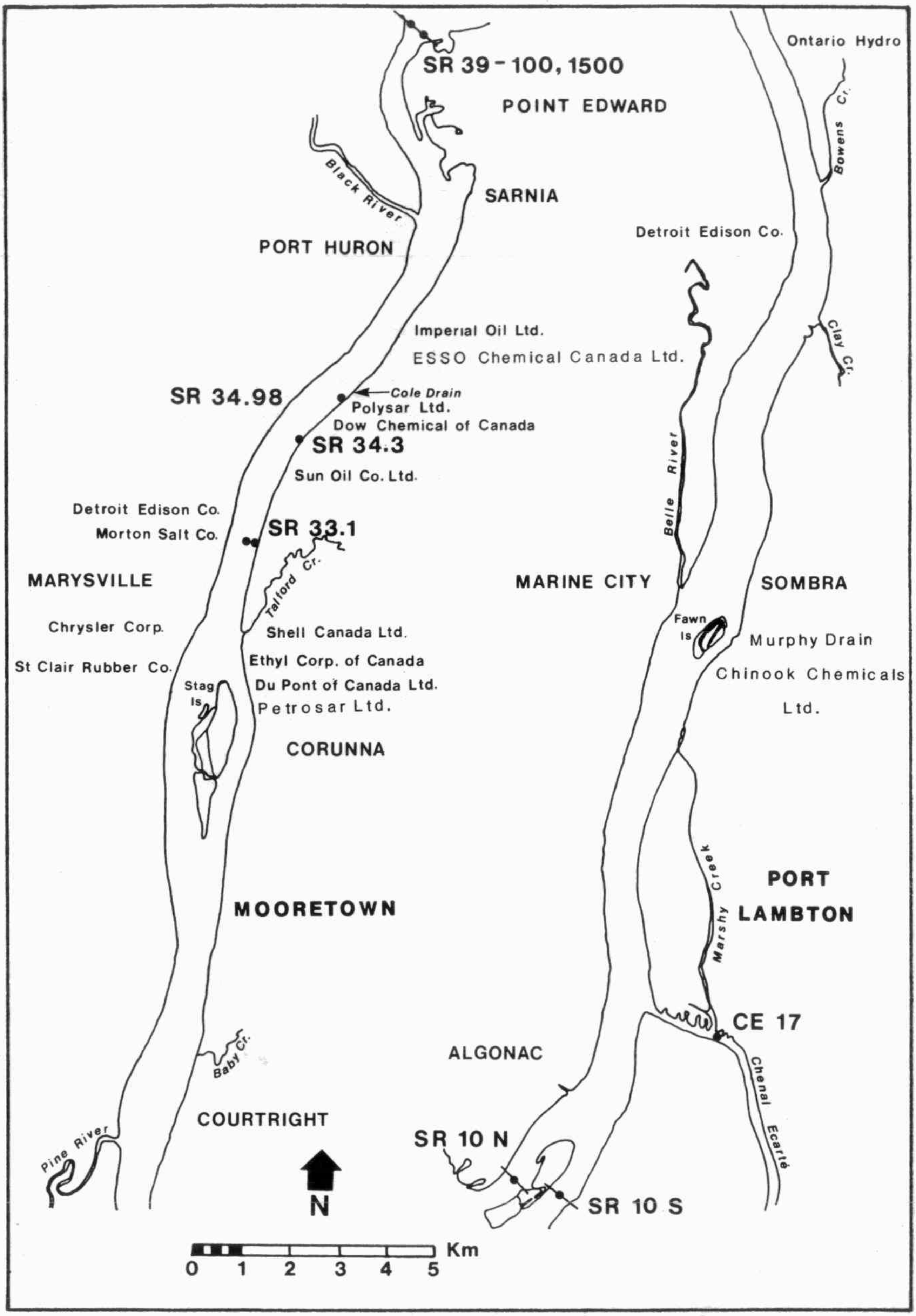

FIGURE 2: St. Clair River sampling locations

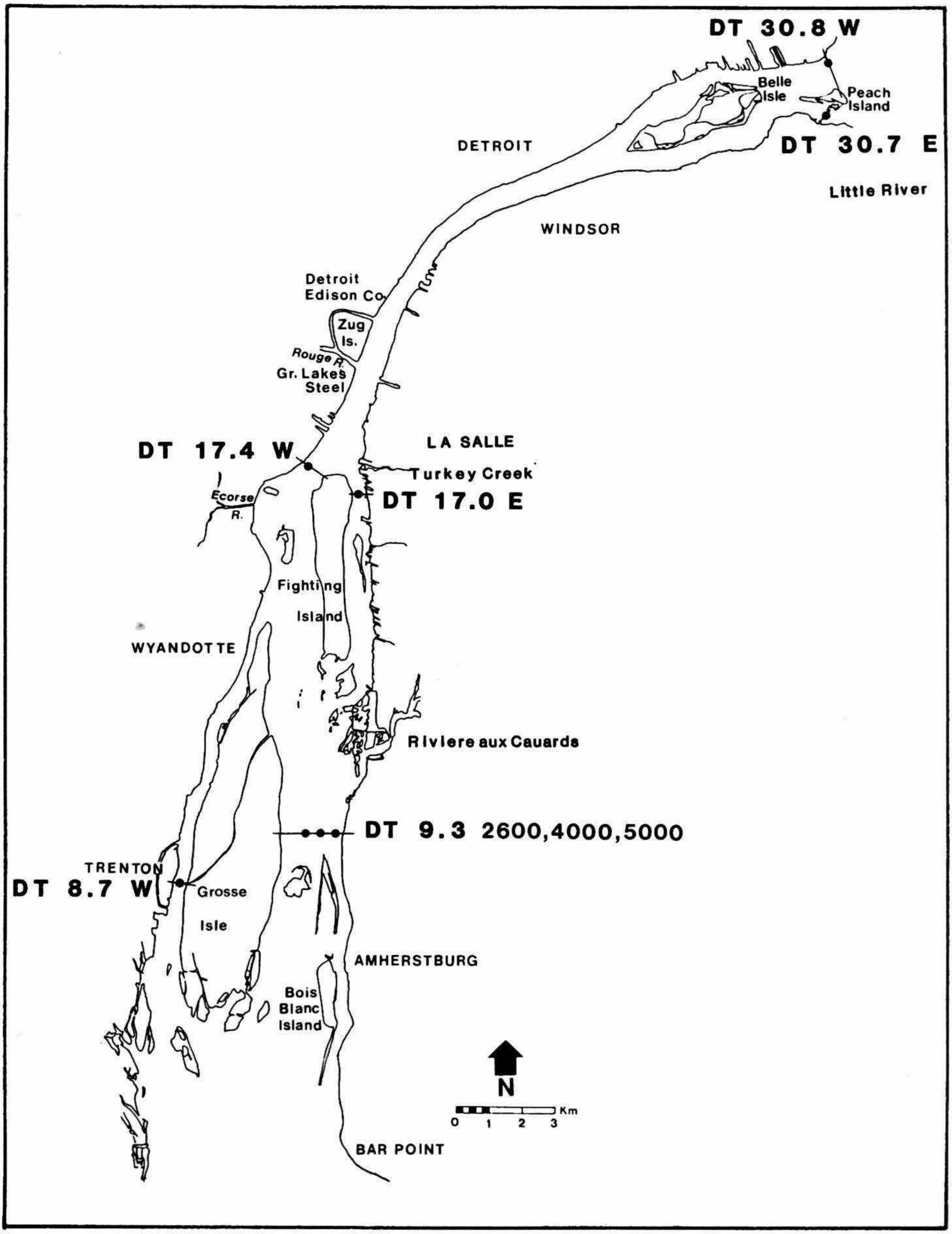

FIGURE 3: Detroit River sampling locations

Time-composited*, whole (unfiltered) water samples were collected from mid-depth using a March 5C-MD submersible pump and handled according to procedures outlined in "A Guide to the Collection and Submission of Samples for Laboratory Analysis" (MOE, 1985). Simultaneously, suspended solid (particulate) samples were collected by pumping water from mid-depth through a continuous-flow Westfalia centrifuge to obtain a minimum of 25 grams (wet weight) of solids.

Polychlorinated biphenyls (PCBs), chlorinated aromatics [hexachlorobenzene (HCB), octachlorostyrene (OCS)], and heavy metals [iron (Fe), mercury (Hg), lead (Pb), zinc (Zn)] were analyzed in both water and suspended sediment samples. Additionally, total phosphorus (TP), dissolved organic carbon (DOC), conductivity, chloride (Cl^-), and suspended solids (RSP) were measured in unfiltered water while centrifuged particulates were analyzed for solvent extractables and total organic carbon (TOC). Analysis for each parameter was conducted in accordance with standard procedures described in the "Handbook of Analytical Methods for Environmental Samples" (MOE, 1983) employed by the Ministry of the Environment main laboratory in Rexdale.

Statistical evaluation of data included the calculation of arithmetic means and standard deviations of contaminants concentrations for each sampling location. Interpretive comparisons were made both graphically and by means of analysis of variance (ANOVA). The concentration data was also used to estimate loadings in whole water based on contaminants measured in suspended particulates for those parameters not routinely detected in water.

Parameters which were not detected in suspended particulate samples were assigned a value of one-half the method detection limit (MDL). This convention was used in instances where values for PCBs, HCB and OCS were below the MDL of 20 ng/g, 1 ng/g and 1 ng/g respectively.

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* half-hourly grabs during the period of centrifugation (usually 3-4 hours).

5.0 RESULTS

5.1 Contaminants in Suspended Solids

5.1.1 St. Clair River

Upwards of 2500 litres of river water were centrifuged to obtain sufficient particulate material for analyses. This quantity of solids enabled reliable quantification, with measurable levels of mercury, HCB, OCS and total PCBs being obtained at nearly all sampling locations. All concentrations are on a dry weight basis.

Contaminant levels in centrifuged particulates (Table 1) were very dependent on the proximity of sampling stations to sources. Total organic carbon (88.5 mg/g), Hg (0.40 µg/g), Zn (109 µg/g), HCB (535 ng/g) and total PCBs (41.3 ng/g) were locally elevated in the "Chemical Valley" area.

OCS levels were elevated along the eastern (Ontario) shore, primarily in the lower reaches of the St. Clair River (i.e. SR10S-42.3 ng/g; CE17-21.7 ng/g). However, no apparent source was evident in the Sarnia area. PCB values peaked adjacent to industry at Sarnia but at times fell to levels at or below the method detection limit (20 ng/g) downriver in the delta area. The mean HCB value of 28.6 ng/g at SR39-1500 is surprising, since water from this control station at the outlet of Lake Huron should be relatively contaminant free. In fact, three cruises yielded <1 ng/g values with only a single (113 ng/g) value above the detection limit. The latter elevated value corresponded to a rain and storm event which occurred at Sarnia several days earlier, and may have resulted from resuspension of bottom sediments or high urban runoff.

A number of parameters remained at background (headwater) levels for the entire extent of the river. Analysis of variance using the procedure of El-Shaarawi and Kwiatkowski (1977) confirmed this statistically, as solvent extractables, total phosphorus and iron did not vary significantly between stations. Inputs at Sarnia did

TABLE 1: **MEAN CONTAMINANT CONCENTRATIONS IN SUSPENDED SOLIDS, 1984.**
Values are mean and standard deviation of 4 surveys, unless otherwise indicated.

Sample Location	Solvent Extractables (mg/g)	Total Org. Carbon (mg/g)	Total Phos. (mg/g)	Iron (mg/g)	Lead (ug/g)	Mercury (ug/g)	Zinc (ug/g)	HCB (ng/g)	OCS (ng/g)	PCBs (ng/g)
St. Clair River:										
SR39-100	9.0±1.0	76.3±33.1	1.25±0.4	20.7±0.06	26.0±4.4	0.04±0.01	86.1±12.2	<1.0	0.67±0.3	<20
SR39-1500	6.9±4.5	48.0±12.8	1.08±0.4	16.3±4.8	19.8±54	0.20±0.3	76.3±15.2	28.6±56.3	1.6±2.0	<20
SR33.1-SR34.98[1]	6.4±6.7	88.5±30.8	0.85±0.5	19.0±1.8	28.3±9.1	0.40±0.5	109.3±44.7	535.3±880	1.6±0.8	41.3±47.3
SR10N	9.3±7.0	43.8±10.4	0.78±0.2	19.0±2.5	23.0±2.6	0.09±0.05	81.1±5.6	48.8±26.1	6.5±3.5	13.8±7.5
SR10S	6.0±3.3	46.5±17.0	0.83±0.2	16.0±1.8	40.0±11.1	0.27±0.08	81.5±19.2	62.0±89.4	42.3±59	27.5±35
CE17	5.9±3.7	44.8±12.6	0.93±0.2	18.3±2.8	41.8±18.8	0.28±0.14	83.0±13.8	37.8±27.5	21.7±17.2	<20
Detroit River:										
DT30.8W	8.9±10.0	68.5±4.0	1.4±0.3	25.3±4.4	52.0±11.3	0.13±0.05	120.0±8.2	2.8±0.5	0.8±0.4	428±801.8
DT30.7E	11.6±8.3	66.3±5.4	1.5±0.5	26.0±5.9	38.3±1.7	0.32±0.14	111.0±15.1	4.5±2.4	2.5±2.1	13.8±7.5
DT17.4W[2]	15.2±12.2	62.7±22.9	1.7±0.6	29.7±4.2	122.5±66.1	0.45±0.21	317.0±165.1	6.9±6.2	2.3±6.2	499±350
DT17.0E[2]	4.5±3.8	47.7±14.1	1.1±0.08	27.2±3.6	53.8±18.1	0.44±0.15	147.0±8.2	10.2±3.3	2.2±1.1	20±8.4
DT8.7W	5.6±2.8	47.8±11.0	1.08±0.9	30.0±2.5	72.8±28	0.48±0.25	213.0±69.5	9.8±3.1	1.9±1.5	204±176
DT9.3-2600	2.7±1.4	39.0±18.8	0.9±0.08	27.0±4.8	44.0±7.5	0.47±0.07	118.0±19.7	11.5±8.7	3.0±1.8	65.0±41.4
DT9.3-4000	3.8±1.5	40.4±10.0	0.9±0.1	25.0±3.7	39.6±4.7	0.44±0.03	117.6±24.1	12.4±9.0	3.2±1.8	15.0±7.1
DT9.3-5000	3.5±2.5	42.8±15.2	0.9±0.05	26.8±3.9	40.3±2.8	0.43±0.15	115.0±5.8	19.0±12.6	3.0±1.7	32.5±6.5

1. Mean of single samples taken during last survey at: SR33.1 (20 + 200 m offshore)
SR34.3 (20 m offshore)
SR34.98 (60 m offshore)

2. Includes duplicate samples taken on each survey.

not appear to significantly impact concentrations of these parameters (Table 1). However, mean levels of Pb, Hg and OCS were significantly higher ($\alpha \leq 0.05$) at station CE17 than at station SR10N, indicative of upstream inputs along the Ontario shoreline. Results of ANOVA are presented in Table A1 and in Figures A1 - A5 in the Appendices.

5.1.2 Detroit River

Lateral distribution of contaminated suspended material in the Detroit River differed from the spatial trends observed in the St. Clair River (Figures A1-A5). Primary inputs appeared to be located along the western (Michigan) shore, particularily in the Detroit/River Rouge area. Suspended particulates from station DT17.4W, downstream of a highly industrialized corridor, contained significantly higher ($\alpha \leq 0.05$) levels of solvent extractables (15.2 mg/g), Pb (122.5 µg/g), Zn (317 µg/g), TP (1.7 mg/g) and PCBs (499 ng/g) than most other locations.

HCB appeared to be somewhat more elevated along the eastern shoreline, possibly corresponding to eastern (Ontario) sources in the St. Clair River. Station DT9.3-5000, located near the Detroit River mouth and adjacent to the eastern shore had significantly higher levels of HCB ($\alpha \leq 0.20$) than other Detroit River stations.

Duplicate sample results from Detroit River Stations are presented in Table A2. In most cases, percent difference between replicates was less than 10%. Exceptions to this were noted for solvent extractables, HCB and PCBs and may somewhat temper interpretive strength for these parameters.

Levels encountered at the Detroit River head cannot be considered background or control concentrations. Results from ANOVA indicated significant increases ($\alpha \leq 0.05$) over background concentrations observed at the head of the St. Clair River for PCBs, Fe, Pb, Hg, Zn

and TP. Of note are the unexpectedly high PCB concentrations measured at DT30.8W (428 ng/g). This indicates a potential source(s) in Lake St. Clair or the upper Detroit River, likely originating from the western shore. While 3 of 4 samples obtained at DT30.8W exceeded method detection limits for total PCBs, this elevated arithmetic mean is largely attributed to a single measured value of 1630 ng/g during the last cruise. Meteorological data do not indicate precipitation at or near the time of sampling; however, the value may result from an episodic point/non-point source discharge and warrants further investigation. Correspondingly high TOC values may partially explain the PCB level observed. Kaiser et al. (1985) noted that increased organic carbon content of suspended particulates resulted in increased adsorption of hydrophobic organic compounds.

5.2 Contaminants in Whole Water

5.2.1 St. Clair River

Mean contaminant concentrations measured in whole water samples are presented in Table 2. Values generally reflected the relative proximity of stations to point sources and were influenced by lateral and downstream distances from these sources.

Several contaminants of interest were at or below method detection limits [Hg (0.01 µg/L); Pb (0.003 mg/L); HCB and OCS (1 ng/L); total PCBs (20 ng/L)] in most whole water samples. Elevated concentrations of these contaminants in suspended material from locations at and downstream of point sources (SR33.1 - SR34.98; SR10N; SR10S; CE17) indicates that contaminants were present in the whole water samples, but at levels too low to accurately quantify.

Oliver (1986) illustrated a significant correlation between octanol/water (K_{OW}) and organic-carbon corrected partition coefficients (K_{OC}). Utilizing total organic carbon (TOC) values for particulates, contaminant levels measured on suspended

TABLE 2: **MEAN CONTAMINANT CONCENTRATIONS IN WHOLE WATER SAMPLES, 1984**

Values are mean and standard deviation of 4 surveys unless otherwise indicated.

Sample Location	Chloride (mg/L)	DOC (mg/L)	Suspended Solids (mg/L)	Total Phosphorus (mg/L)	Iron (mg/L)	Lead (mg/L)	Mercury (ug/L)	Zinc (mg/L)	HCB* (ng/L)	OCS* (ng/L)	PCBs* (ng/L)
St. Clair River:											
SR39-100	6.4±0.8	1.6±0.13	4.3±4.6	0.02±0.02	0.08±0.09	<0.003	<0.01	0.001±0.001	<0.02	0.003	<0.20
SR39-1500	6.0±0.6	4.1±4.9	7.8±10.1	0.008±0.004	0.14±0.02	<0.003	<0.01	0.002±0.001	0.69	0.02	<0.20
SR33.1-SR34.98[1]	11.0±8.6	1.5±0.05	7.8±8.8	0.009±0.003	0.14±0.12	<0.003	0.011	0.003±0.001	8.97	0.02	0.69
SR10N	6.3±0.5	1.7±0.3	8.7±3.6	0.009±0.003	0.13±0.06	<0.003	<0.01	0.002±001	1.32	0.10	0.37
SR10S	9.1±1.4	1.7±0.2	7.7±2.4	0.009±0.001	0.10±0.05	<0.003	<0.01	0.002±0.002	1.54(5.0)	0.56	0.68
CE17	9.9±2.2	1.7±0.06	26.1±44.3	0.034±0.03	0.60±1.1	<0.003	0.1	0.003±0.004	1.66(1.0)	0.69	<0.20
Detroit River:											
DT30.8W	9.0±2.4	1.8±0.13	9.5±8.5	0.014±0.005	0.17±0.14	<0.003	<0.01	0.002±0.001	0.06	0.011	9.03
DT30.7E	9.1±2.1	1.9±0.13	8.8±5.1	0.02±0.02	0.33±0.40	<0.003	<0.01	0.002±0.002	0.094	0.029	0.29
DT17.4W[2]	11.4±0.9	2.0±0.14	18.5±12.3	0.03±0.01	0.46±0.21	<0.003	<0.01	0.008±0.003	0.22	0.05	15.55
DT17.0E[2]	9.7±1.3	1.8±0.2	10.7±5.2	0.02±0.01	0.28±0.17	<0.003	<0.01	0.003±0.001	0.28	0.04	0.54
DT8.7W	12.1±0.3	2.0±0.08	21.4±7.9	0.03±0.02	0.52±0.19	<0.003	<0.01	0.007±0.001	0.37	0.05	7.76
DT9.3-2600	8.4±0.1	1.8±0.08	18.7±8.5	0.02±0.004	0.33±0.11	<0.003	<0.01	0.005±0.002	0.45	0.08	2.54
DT9.3-4000	8.4±0.6	1.8±0.07	12.4±5.4	0.02±0.004	0.37±0.15	<0.003	<0.01	0.006±0.008	0.39	0.06	0.48
DT9.3-5000	9.3±0.9	1.8±0.2	12.4±5.4	0.03±0.01	0.44±0.25	<0.003	<0.01	0.002±0.001	0.59	0.06	1.0

1. Mean of single samples taken at: SR33.1 (20 + 200 m offshore)
   SR34.3 (20 m offshore)
   SR34.98 (60 m offshore)
2. Includes duplicate samples taken on each survey.

* values predicted from concentrations on suspended solids and derived from equations of Oliver (1986).

()values in brackets are actual whole water mean values; all others are below method detection limits for water (1 ng/L for HCB & OCS; 20 ng/L for PCBs)

particulates and organic carbon corrected partition coefficients, estimates of dissolved (aqueous) contaminant levels and whole water concentrations were obtained. Application of this method to particulate-associated HCB, OCS and PCB levels also provided insight into their partitioning behaviour. (For details of this method, refer to Appendices, page 43).

Table 3 shows the estimated contributions of dissolved and particulate phases to whole water concentrations. Most predicted values were near or below the routine method detection limits for 1 litre samples, and thus compared favourably with observed laboratory results. The one exception to reported whole water values was HCB (predicted to be 8.97 ng/l, observed as <1 ng/l). This discrepancy may have arisen due to comparison of composited half-hourly grab samples for water versus continuous, time-composited particulate samples. It is unclear why HCB is the only parameter for which this has occurred; however, this may be due to non-representative samples or an artifact of analysis.

Spatially, the predicted concentrations of most organics in water increased from the head to the mouth of the St. Clair River. Also, notable elevations near the Sarnia "Chemical Valley" occurred for Cl^- and HCB, two by-products of the manufacture of chlorinated compounds. PCBs and Hg concentrations also increased in this section of the river. Mercury inputs are probably associated with the previous method (mercury brine cell) of chlorine manufacture. Figures 4-6 illustrate these spatial trends for HCB, OCS and PCBs.

Analysis of variance indicated some significant differences between stations for whole water contaminant concentrations. Table A3 summarizes the ANOVA results. For most parameters, there were no significant differences between stations on the St. Clair River ($p \le 0.05$ or 0.10) and these occupied a single cluster. Chloride levels at stations SR10S and CE17 were significantly elevated due to upstream discharges at Sarnia. As shown by Hamdy and Kinkead (1979) these inputs remain close to the Canadian shore. ANOVA was not conducted on estimated parameters; however, OCS did appear to be

TABLE 3: RELATIVE CONTRIBUTIONS TO WHOLE WATER CONTAMINANT LEVELS BY DISSOLVED (AQUEOUS)AND PARTICULATE FRACTIONS*

Location	Parameter	Dissolved Fract.[1]		Particulate Fract.[2]		Whole Water[3]
		(ng/L)	% Total	(ng/L)	% Total	(ng/L)
St. Clair River						
SR39-100	HCB	-		-		
	OCS	0.0002	6.5	.0029	93.5	0.003
	PCBs	-		-		
SR39-1500	HCB	0.47	68.1	0.22	31.9	0.69
	OCS	0.01	50.0	0.01	50.0	0.02
	PCBs	-		-		
SR33.1-SR34.98	HCB	4.8	53.5	4.17	46.5	8.97
	OCS	0.01	29.4	0.01	70.6	0.02
	PCBs	0.37	67.6	0.32	46.4	0.69
SR10N	HCB	0.9	68.2	0.421	31.8	1.32
	OCS	0.04	39.4	0.06	60.6	0.10
	PCBs	0.25	67.6	0.12	32.4	0.37
SR10S	HCB	1.06	68.8	0.48	31.2	1.54
	OCS	0.23	41.1	0.33	58.9	0.56
	PCBs	0.47	69.1	0.21	30.9	0.68
CE17	HCB	0.67	40.4	0.99	59.6	1.66
	OCS	0.12	17.4	0.57	82.6	0.69
	PCBs	-		-		
Detroit River						
DT30.8W	HCB	0.03	52.6	0.03	47.4	0.06
	OCS	0.003	27.3	0.01	62.7	0.01
	PCBs	4.96	54.9	4.07	45.1	9.03
DT30.7E	HCB	0.05	57.4	0.04	42.6	0.09
	OCS	0.01	31.0	0.02	69.0	0.03
	PCBs	0.17	58.6	0.12	41.4	0.29
DT17.4W	HCB	0.09	40.9	0.13	59.1	0.22
	OCS	0.01	20.0	0.04	80.0	0.05
	PCBs	6.32	40.6	9.23	59.4	15.55
DT17.0E	HCB	0.17	60.7	0.11	39.3	0.28
	OCS	0.02	50.0	0.02	50.0	0.04
	PCBs	0.33	61.1	0.21	38.9	0.54
DT9.3-5000	HCB	0.35	59.3	0.24	40.7	0.59
	OCS	0.02	33.3	0.04	66.7	0.06
	PCBs	0.60	60.0	0.40	40.0	1.0
DT9.3-4000	HCB	0.24	61.5	0.15	38.5	0.39
	OCS	0.02	33.3	0.04	66.7	0.06
	PCBs	0.29	60.4	0.19	39.6	0.48
DT9.3-2600	HCB	0.23	51.1	0.22	48.9	0.45
	OCS	0.02	25.0	0.06	75.0	0.08
	PCBs	1.32	51.8	1.22	48.2	2.54
DT8.7W	HCB	0.16	43.2	0.21	56.8	0.37
	OCS	0.01	20.0	0.04	80.0	0.05
	PCBs	3.39	43.7	4.37	56.3	7.76

1. Dissolved fraction estimated from particulate fraction using method of Oliver (1986). For example, see Appendices (Pg. 43).
2. Particulate fraction contaminant concentrations were normalized to an equivalent volume of water by multiplying particulate-associated contaminant concentration (Table 1) by the corresponding suspended solids concentration (Table 2).
3. Whole water concentration obtained by summation of dissolved and particulate phases.
-: unable to estimate since below method detection limits.

FIGURE 4: HCB in whole water (ng/L)

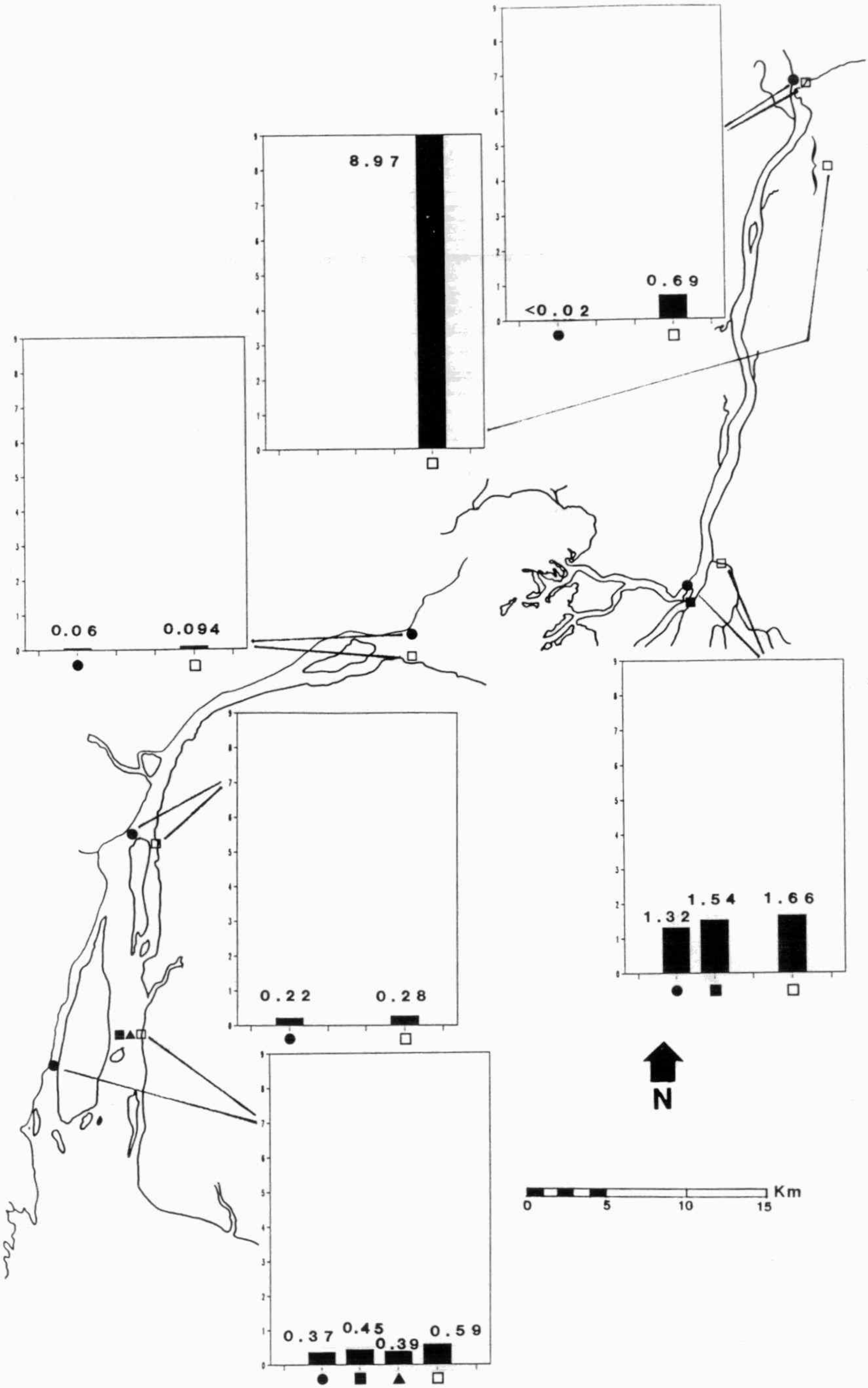


FIGURE 5: OCS in whole water (ng/L)

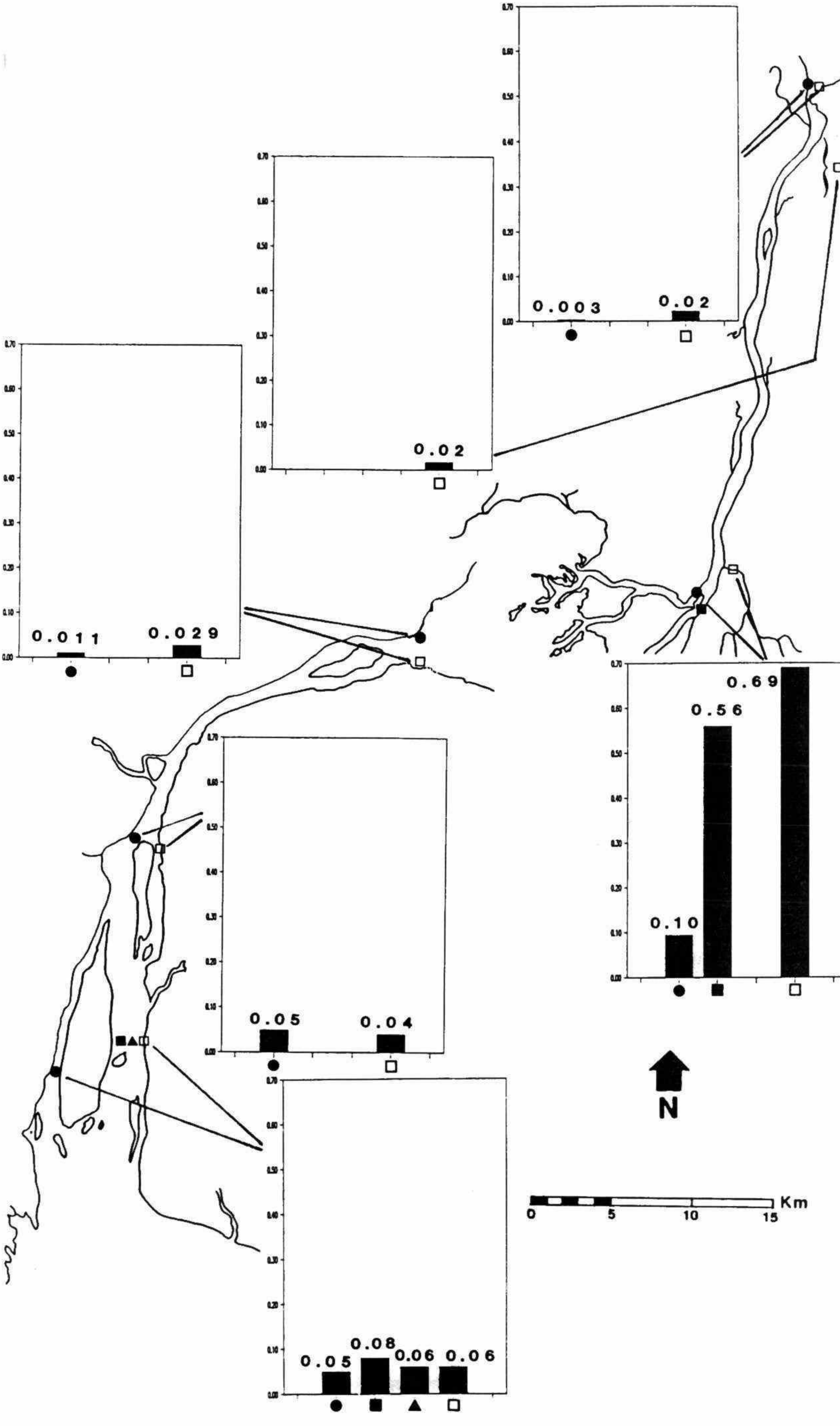
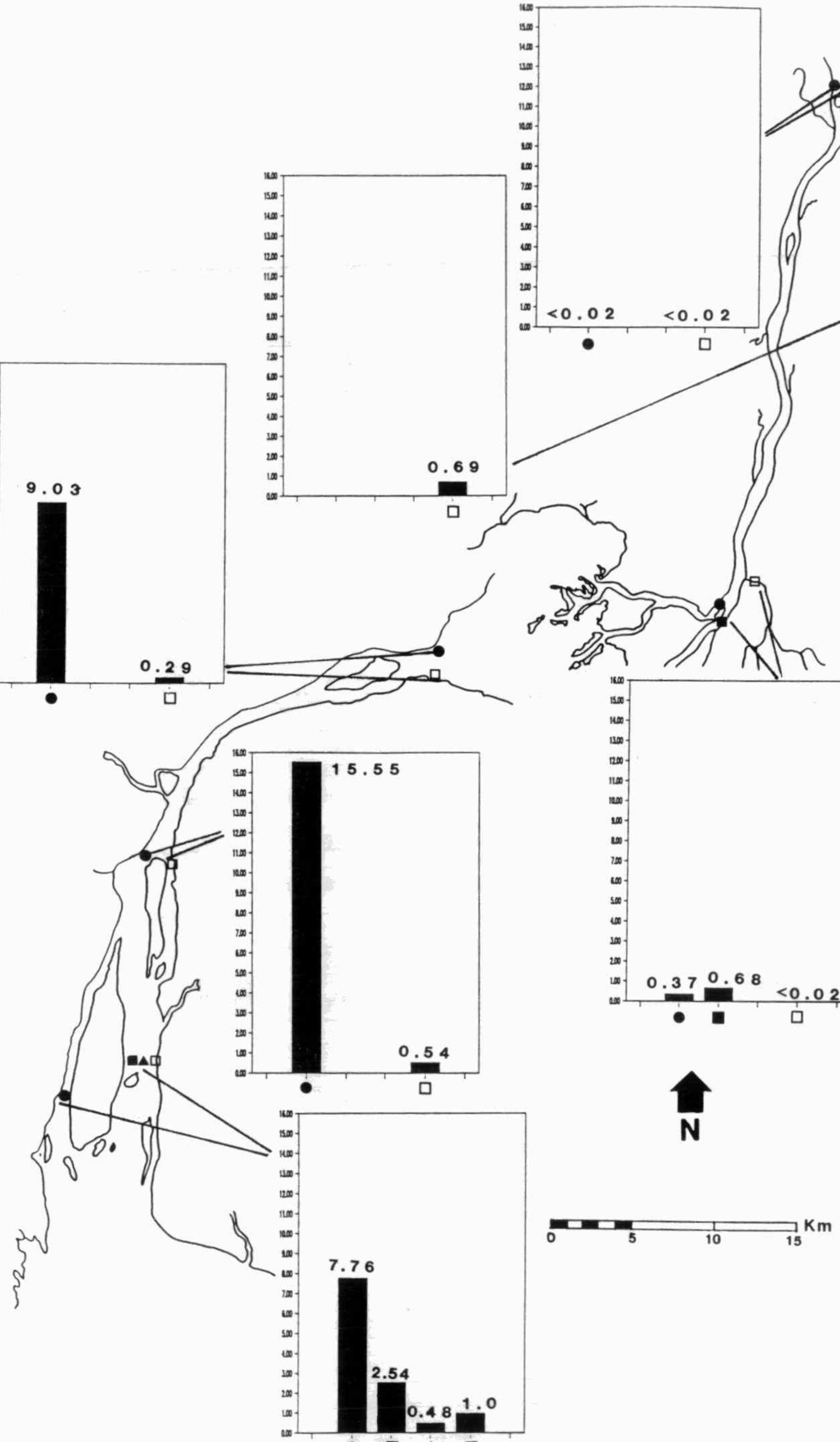


FIGURE 6: PCBs in whole water (ng/L)



significantly higher in South Channel and Chenal Ecarte waters (stations SR10S and CE17) than along the U.S. shoreline (station SR10N). HCB would be expected to follow a similar pattern in whole water based on inputs in the "Chemical Valley" and levels found in the particulates in the lower river; however no distinct lateral gradient was detected in the estimated whole water concentrations (Table 4).

5.2.2 Detroit River

Whole water contaminant levels in the Detroit River were generally of similar magnitude to those measured in the St. Clair River. A strong affinity for the shore of origin was observed, as in the St. Clair River, with a minimal tendency for transboundary pollution.

Table A4 summarizes field duplicate and blank results for whole water samples. Generally, percent differences for duplicates were below 10%; however, larger differences were observed on at least one occasion for suspended solids, total phosphorus, iron and zinc. These differences may be due to a combination of factors, including field and laboratory error. Concentrations in blanks were usually an order of magnitude or more lower than in actual field samples.

Measured values and estimated concentrations of organics using the method of Oliver (1986) are presented in Table 2. Results indicated a trend of elevated concentrations along the western (Michigan) shore, increasing with distance downstream. RSP (9.5 to 21.4 mg/L), Chloride (9.0 to 12.1 mg/L), TP (0.014 to 0.030 mg/L), Fe (0.17 to 0.52 mg/L) and Zn (0.002 to 0.007 mg/L) illustrated this trend from the headwaters to the lower river. A similar trend was observed for RSP (8.8 to 12.4 mg/L), TP (0.02 to 0.03 mg/L), Fe (0.33 to 0.44 mg/L) and PCBs (0.29 to 1.0 ng/L) along the eastern (Ontario) shore. HCB and OCS also increased somewhat (2 to 6-fold) from the inlet of the river to the outlet along the Ontario shoreline.

Table 4 provides evidence that transboundary pollution does not occur. This is particularly evident from the estimated total PCB

TABLE 4: **COMPARISON OF CONTAMINANT LEVELS BY SHORELINE (mean concentrations, units as indicated)**

PARAMETER	St. Clair River - Head		St. Clair River - Mid		St. Clair River - Mouth	
	U.S. Shore SR39-100	Can. Shore SR39-1500	U.S. Shore NM	Can. Shore SR33.1-SR34.98	U.S. Shore SR10N	Can. Shore CE17
WHOLE WATER						
Susp. Solids (mg/L)	4.3	7.8	-	7.8	8.7	26.1
DOC (mg/L)	1.6	4.1	-	1.5	1.7	1.7
Chloride (mg/L)	6.4	6.0	-	11.0	6.3	9.9
Tot. Phos. (mg/L)	0.02	0.01	-	0.01	0.01	0.03
Iron (mg/L)	0.08	0.14	-	0.14	0.13	0.60
Lead (mg/L)	<0.003	<0.003		<0.003	<0.003	<0.003
Mercury (µg/L)	<0.01	<0.01	-	0.011	<0.01	0.01
Zinc (µg/L)	0.001	0.002	-	0.003	0.002	0.003
HCB (ng/L)	<0.02*	0.69*	-	8.97*	1.32*	1.66*
OCS (ng/L)	0.003*	0.022*	-	0.017*	0.09*	0.69*
PCB (ng/L)	<0.20*	<0.20*	-	0.69*	0.37*	<0.20*
SUSPENDED SOLIDS						
T.O.C. (mg/g)	76	48	-	88.	44	45
Total Phos. (mg/g)	1.3	1.1	-	0.9	0.8	0.9
Iron (mg/g)	21	16	-	19	19	18
Lead (mg/g)	26	20	-	28	23.	42
Mercury (µg/g)	0.04	0.2	-	0.40	0.09	0.30
Zinc (µg/g)	86	76	-	109	81	83
Solvent Ext. (mg/g)	9.0	6.9	-	6.4	9.3	5.9
HCB (ng/g)	<1.0	29	-	535	49	38
OCS (ng/g)	0.7	1.7	-	1.6	7	22
PCB (ng/g)	<20	<20	-	41.3	13.8	<20

PARAMETER	Detroit River - Head		Detroit River - Mid		Detroit River - Lower	
	U.S. Shore DT 30.8W	Can. Shore DT 30.7E	U.S. Shore DT 17.4W	Can. Shore DT 17.0E	U.S. Shore DT 8.7W	Can. Shore DT 9.3-5000
WHOLE WATER						
Susp. Solids (mg/L)	9.4	8.8	18.9	10.2	21.4	17.8
DOC (mg/L)	1.8	1.8	2.0	1.8	2.0	1.8
Chloride (mg/L)	9.0	9.1	11.3	9.9	12.1	9.3
Tot. Phos. (mg/L)	0.01	0.02	0.04	0.02	0.03	0.03
Iron (mg/L)	0.17	0.33	0.46	0.25	0.52	0.44
Lead (mg/L)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Mercury (µg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zinc (µg/L)	0.002	0.001	0.007	0.003	0.007	0.002
HCB (ng/L)	0.057	0.094*	0.22*	0.28*	0.37*	0.59*
OCS (ng/L)	0.011*	0.029*	0.05*	0.040*	0.05*	0.060*
PCB (ng/L)	9.03*	0.29*	15.55*	0.54*	7.76*	1.0*
SUSPENDED SOLIDS						
T.O.C. (mg/g)	69	66	63	48	48	39
Total Phos. (mg/g)	1.4	1.5	1.7	1.1	1.1	0.9
Iron (mg/g)	25	26	30	27	30	27
Lead (mg/g)	52	38	123	54	73	40
Mercury (µg/g)	0.13	0.32	1.45	0.44	0.48	0.43
Zinc (µg/g)	120	111	317	147	213	115
Solvent Ext. (mg/g)	8.9	11.6	14.2	4.5	5.6	3.5
HCB (ng/g)	3	5	7	10	10	19
OCS (ng/g)	1	3	2	2	2	3
PCB (ng/g)	428	14	499	20	204	33

* estimated by method of Oliver (1986)

NM - not measured

levels (Figure 6). Depending on the location and phase, total PCB concentrations along the western shore were 8 to 31 times those estimated for the eastern shoreline. It should be noted that these differences may not be significant however, as values were estimated and were at or below the method detection limit of 1 ng/L.

Results of ANOVA for Detroit River stations indicated significant lateral differences in contaminant levels. Western stations DT17.4W, DT8.7W and DT9.3-2600 were generally clustered together, having higher concentrations than corresponding eastern shore stations.

6.0 DISCUSSION

6.1 Estimation of Loadings

6.1.1 Hydrodynamic/Meterological Characteristics

For purposes of loading estimation, each river was divided into three discrete compartments: 'head', 'mid' and 'mouth'. These segments were based on zones of unique flow characteristics or the presence of suspected major contaminant sources. The St. Clair river was separated into three segments; the upper compartment ('head') acted on by Lake Huron wind conditions; the 'mid' receiving industrial inputs from the Sarnia "Chemical Valley", and the 'mouth' consisting of a wide delta entering Lake St. Clair. Similarly, the Detroit River was comprised of 'head', 'mid' and 'mouth' segments subject to influences from Lake St. Clair, contaminant inputs in the Detroit/Windsor area and Lake Erie, respectively.

Flow rate transects (Figure 1) established by the National Oceanic and Atmospheric Administration (NOAA) provided average daily flow rates. Whole water concentrations (Table 2) representing the sum of aqueous and particulate fractions were measured or estimated and mean loading values calculated for each compartment.

Average flow rates between transects varied minimally due to a lack of significant lateral inputs (J. Derecki, NOAA, pers. comm.). As an example, cumulative flows from tributaries entering either river from the Canadian shore enhanced river flow rates by <1% (P.B. Kauss, MOE; pers. comm.); however, flow rates may have been significantly impacted over the short-term by local weather conditions. The mid-to lower reaches of the Detroit River were observed to be greatly influenced by winds originating in Lake Erie. Enhancement or reduction of flow rates in these compartments was dependent on prevailing wind directions. Winds from the south or south-east were found to reduce flow rates in the lower Detroit River for short periods of time.

Studies by Quinn (1976) have revealed Detroit River flow rate variances of $\pm$ 3% ($\pm$ 170m^3/sec) south of Wyandotte, Michigan, while a lower variance of $\pm$ 1% ($\pm$ 60m^3/sec) was seen upstream of the same location (Figure 3). Temperature, wind and precipitation records from Environment Canada and flow rate modelling by NOAA for the study period revealed an apparent correlation between low average daily flows in the Detroit River and Lake Erie winds from the southeast direction. This relationship was more predominant in the late fall-through-spring period, when elevated wind speeds were able to retard flow rates. Average flow during periods of south-easterly winds for May and November 1984 were 4.2 and 3.6 percent below their respective monthly averages (Table 5).

The St. Clair River was similarly influenced by wind and storm events. Flow rates in the lower St. Clair River were 1.2 to 3.8 percent below monthly means during periods of southerly winds from Lake St. Clair. Conversely, winds from the north passing over Lake Huron enhanced flows by 1.1 to 8.5 percent above monthly means.

Contaminant levels and precipitation appeared to be positively correlated, as a number of parameters exhibited wet-weather concentrations 2 to 3 times higher than observed under dry conditions. Short-term elevations not representative of dry weather conditions were observed to occur for Fe, RSP, Zn, Pb, solvent

TABLE 5: **DETROIT AND ST. CLAIR RIVERS FLOW ENHANCEMENT/ REDUCTION RESULTING FROM WINDS OVER LAKES ERIE, ST. CLAIR AND HURON**

ST. CLAIR RIVER - Measured at Head and Mouth

1984 Month	Monthly Means m^3/s		Specific Means From North	From South	% Increase (n)		% Reduction (n)	
	Head	Mouth	Head	Mouth	Head		Mouth	
May	6421	6420	6660	6237.5	3.7	(4)	2.9	(6)
June	6435	6435	6582.5	6350.3	2.3	(6)	1.3	(8)
July	6568	6568	6682.8	6489.8	1.7	(5)	1.2	(16)
August	6520	6520	6673	6372	2.4	(10)	2.3	(11)
September	6493	6493	6691.8	6309.3	3.1	(6)	2.8	(12)
October	6471	6471	6543.4	6284.8	1.1	(7)	2.9	(4)
November	6434	6435	6982.5	6193	8.5	(2)	3.8	(14)

DETROIT RIVER - Measured at Wyandotte, Mich. (Lower Detroit River)

1984 Month	Monthly Means m^3/s	Specific Means (south-east direction)	% Reduction	(n)
May	6036	5780.8	4.2	(4)
June	6203	6113.2	1.4	(5)
July	6381	6277.5	1.6	(4)
August	6375	6339.11	0.6	(9)
September	6436	6358.7	1.2	(12)
October	6404	6287.9	1.8	(7)
November	6510	6274.3	3.6	(10)

(n) = number of days in which winds were primarily from specified direction.
Source: Environment Canada, Atmospheric Environment Service, 1984.

extractables and PCBs. However, these concentrations were not immediately observed at all stations following rain events, due to the lag time in downstream transport and the time necessary to complete centrifuging at all stations during each survey.

Strong winds and precipitation recorded at the Sarnia and Windsor meteorological stations on November 11, 1984 during survey 4 produced flow rates 15.1 percent above normal, with suspended solids and iron concentrations in whole water 20 to 30 times greater than measured on other surveys. These observations are graphically represented in figures 7 and 8 for iron and RSP from selected stations.

A rain event on August 18 at Windsor had a relatively minor impact on Detroit River flow rates since winds were light and variable in direction. Contaminant concentrations were significantly affected; however, as Fe and RSP concentrations in whole water samples were elevated 3-to 5 fold respectively, resulting from greater than 6 cm of rain in 24 hours (Environment Canada, 1984). Increased flow rates of 3.4% for 24 hours following this severe rain event were attributed to runoff; however, precipitation during the four surveys (if not coupled with enhancing winds) did not normally produce significant changes in flow rates.

Physical modelling studies (Nettleton, 1986) have confirmed observations by Hamdy and Kinkead (1979) and Kauss and Hamdy (1985) that discharges from the eastern shore of the St. Clair River were mainly confined to a narrow panel adjacent to shore. Aerial photographs of the St. Clair River taken on June 20, 1984 revealed a distinct turbidity plume confined to within approximately 100 m of each shore. These two nearshore panels (each contributing approximately 5% of total flow) were separated by a wide zone of relatively cleaner water.

It has been assumed that for gross loading estimates, panel widths would be determined by the distance of sampling points from shore. Measured contaminant levels were assumed to be representative of a

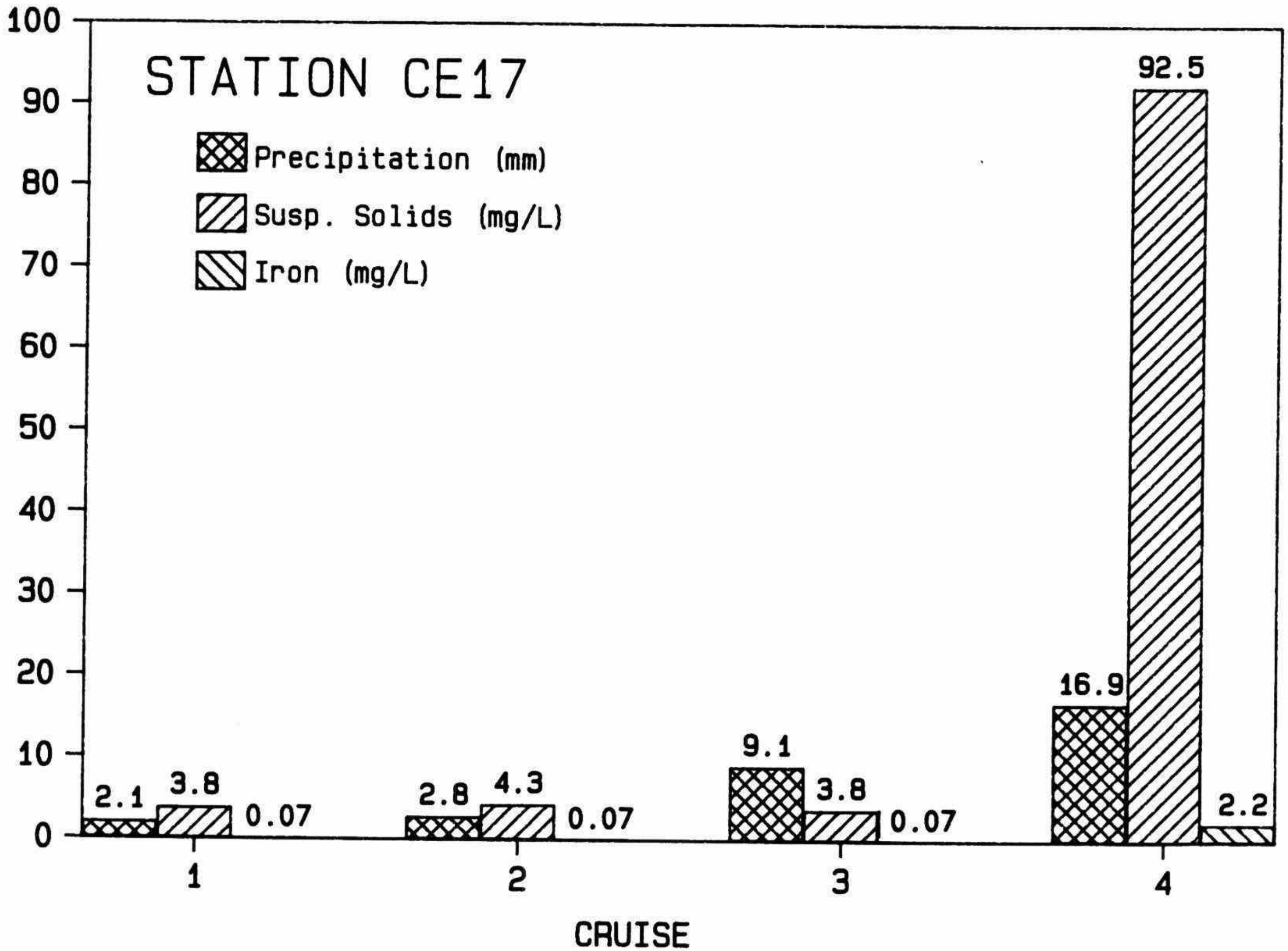


FIGURE 7: Impact of rainfall on iron and suspended solids in whole water samples obtained during 1984--Station CE17

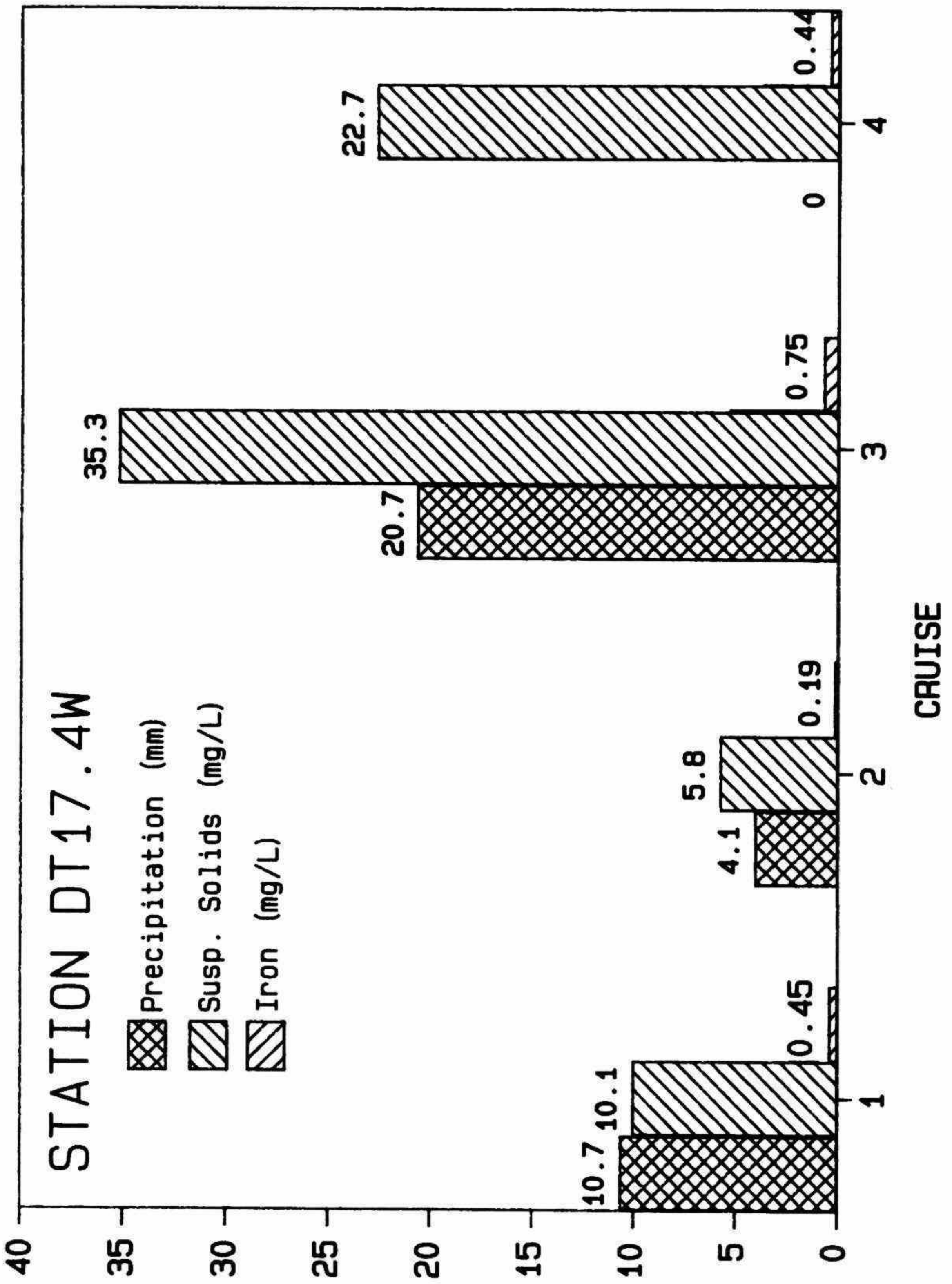


FIGURE 8: Impact of rainfall on iron and suspended solids in whole water samples obtained during 1984--Station DT17.4W

panel extending two times this sampling distance from shore. Estimated values from "K-epsilon" hydrodynamic models (Chan et al., 1986; Ibrahim, 1986; Nettleton, 1986) provided the percent of total flows for each panel. This enabled flow-weighted average contaminant concentrations and loadings to be derived. The fraction of mid-channel flow passing between those panels in the St. Clair River was assumed to contribute minimally to loadings. Samples collected within 200 m from the Canadian shore at the St. Clair 'mid' were considered representative of a 400 m wide panel. This corresponded to approximately 75% of the river discharge volume, the proportion utilized in loading calculations. Stations situated in 3 channels at the St. Clair River 'mouth' were flow-weight averaged and loadings were estimated based on 100% of the flow.

All Detroit River transects utilized 100% of river flow to estimate loadings, based on the assumption of incomplete lateral mixing (Hamdy and Kinkead, 1979; Kauss and Hamdy, 1985). 'Head' and 'mouth' stations were simply flow-weight averaged; however, loadings at the Detroit River 'mid' were calculated somewhat differently. Measured contaminant levels enabled nearshore panel loadings to be estimated; however, the mid-channel flow could not be considered clean. Mid-channel concentrations were estimated using average concentrations measured at the Detroit River 'head'.

By further sectioning each river into compartments, relative changes in loadings between segments provided an understanding of where contaminants enter the system and their ultimate fate. In this way, the importance of Lake St. Clair as a potential sink for contaminants could be assessed through changes occurring between the mouth of the St. Clair River and the head of the Detroit River.

6.1.2 Spatial Distribution of Contaminant Loadings

Based on the above approach which provided representative panel flow volumes, observed contaminant concentrations were flow-weight

averaged for each river segment for parameters measured above detection limits. Parameters at or below method detection limits were estimated from concentrations in suspended solids (Oliver, 1986) and used in loading calculations. Generally, loadings were distributed similarly to contaminant levels, since they were a function of concentrations (Table 6).

The lateral distribution of contaminants is dictated by hydrodynamic characteristics of the receiving water. As such, this effect was observed by sampling along both shorelines and at varying distances from shore.

The Michigan nearshore of the Detroit River has been heavily impacted by industrial and municipal inputs from Detroit and the surrounding area. Local elevations of PCBs in surficial sediments were documented by Hamdy and Post (1985) at Zug Island and Ecorse, upstream of DT17.4W. PCBs were detected in water samples from the Detroit, Ecorse and Trenton Channel areas in 1982 (Kauss and Hamdy, 1985). Kaiser et al. (1985) noted a high and relatively stable PCB_{water}: organic $carbon_{sediment}$ ratio near the western shore, indicating continuous PCB inputs along the extent of the Detroit River. Ratios were observed to increase downstream along the eastern shore, suggesting a release of PCBs from sediments to water and an absence of new inputs. Observed solids data (Table 1) and estimated whole water concentrations (Table 2) are in agreement with this finding.

HCB loadings in whole water estimates from suspended solid concentrations peaked (3.6 kg/day) in the St. Clair River 'mid' section. This area was impacted by discharges from the Sarnia "Chemical Valley". In addition, Cl^- (4.5×10^6 kg/day), zinc (1.2×10^3 kg/day) and PCB (0.3 kg/day) loadings also reached maximum values in this section of the St. Clair River. These peaks, particularly for HCB, may be attributable to waste products in the manufacture of chlorinated solvents and chlorine as well as other compounds in the Sarnia area (Oliver and Bourbonniere, 1985).

TABLE 6: AVERAGE CONCENTRATIONS AND ESTIMATED LOADINGS AT SAMPLE LOCATIONS (Whole Water)

PARAMETER	ST. CLAIR RIVER (HEAD) (SR39.0-100; 1500) Avg. Flow: 621.6 m^3/s* (10% of total)		ST. CLAIR RIVER (MID) SR33.1-SR34.98 Avg. Flow: 4693.5 m^3/s* (75% of total)		ST. CLAIR RIVER (MOUTH) (SR10 N & S; CE17.0) Avg. Flow: 6366 m^3/s* (100% of total)	
	Flow-weighted Average Conc'n	Loadings (kg/day)	Flow-weighted Average Conc'n	Loadings (kg/day)	Flow-weighted Average Conc'n	Loadings (kg/day)
Suspended Solids (mg/L)	6.1 (8)	3.2×10^5	7.8 (4)	3.2×10^6	9.1 (12)	5.0×10^6
Dissolved Organic Carbon (mg/L)	1.6 (8)	8.6×10^4	1.5 (4)	6.0×10^5	1.7 (2)	9.4×10^5
Chloride (mg/L)	6.2 (8)	3.2×10^5	11.0 (4)	4.5×10^6	7.7 (12)	4.2×10^6
Total Phos. (mg/L)	0.014 (7)	7.2×10^2	0.009 (4)	3.6×10^3	0.010 (12)	5.5×10^3
Iron (mg/L)	0.11 (8)	5.8×10^3	0.14 (4)	5.7×10^4	0.14 (12)	7.6×10^4
Lead (mg/L)	0.14@	7.5×10^3	0.17@	6.9×10^4	0.28 @	1.6×10^5
Mercury (ug/L)	0.002@	0.09	0.011 (4)	4.5	0.012 (3)	6.6
Zinc (mg/L)	0.003 (4)	1.3×10^2	0.003 (4)	1.2×10^3	0.002 (2)	1.1×10^3
HCB! (ng/L)	0.35	0.01	8.97	3.6	1.43	0.8
OCS! (ng/L)	0.01	0.0003	0.02	0.07	0.32	0.2
PCBs! (ng/L)	0	0	0.7	0.03	0.5	0.3

! concentrations estimated by method of Oliver (1986).
* Flow rates represent fraction of flow used in estimation of loadings. Remainder of flow assumed to be relatively contaminant free.
(n) Average concentrations based on number (n) of measurements with quantified values.
@ Not detected in whole water; this value represents solid phase contribution only.

TABLE 6: (cont'd)

PARAMETER	DETROIT RIVER (HEAD) (DT30.8W; DT30.7E) Avg. Flow: 6282 m^3/s* (100% of total)		DETROIT RIVER (MID) (DT17.4W; DT17.0E) Avg. Flow 6282 m^3/s* (100% of total)		DETROIT RIVER (MOUTH) (DT9.3E (3); DT8.7W) Avg. Flow: 6282 m^3/s* (100% of total)	
	Flow-weighted Average Conc'n	Loadings (kg/day)	Flow-weighted Average Conc'n	Loadings (kg/day)	Flow-weighted Average Conc'n	Loadings (kg/day)
Suspended Solids (mg/L)	9.3 (8)	5.04 x 10^6	12.02 (15)	6.5 x 10^6	15.2 (17)	8.3 x 10^6
Dissolved Organic Carbon (mg/L)	1.8 (8)	9.8 x 10^5	1.9 (15)	1.0 x 10^6	1.9 (17)	1.0 x 10^6
Chloride (mg/L)	9.0 (8)	4.9 x 10^6	9.8 (15	5.3 x 10^6	9.6 (17)	5.2 x 10^6
Total Phos. (mg/L)	0.013 (8)	7.1 x 10^3	0.019 (11)	1.03 x 10^4	0.025 (16)	1.4 x 10^4
Iron (mg/L)	0.21 (8)	1.14 x 10^5	0.29 (15)	1.6 x 10^5	0.42 (17)	2.3 x 10^5
Lead (mg/L)	0.45@	2.44 x 10^5	0.56@	3.0 x 10^5	0.80 @	4.3 x 10^5
Mercury (ug/L)	0.002@	1.1	0.008 (9)	4.6	0.013 (9)	7.1
Zinc (mg/L)	0.002 (6)	0.1 x 10^3	0.004 (16)	2.2 x 10^3	0.005	2.7 x 10^3
HCB! (ng/L)	0.07	0.04	0.17	0.1	0.45	0.2
OCS! (ng/L)	0.02	0.009	0.03	0.017	0.06	0.03
PCBs! (ng/L)	6.9	3.7	7.1	3.9	3.0	1.6

! Concentrations estimated by method of Oliver (1986).
* Flow rates represent fraction of flow used in estimation of loadings. Remainder of flow assumed to be relatively contaminant free.
(n) Average concentrations based on number (n) of measurements with quantified values.
@ Not detected in whole water; this value represents solid phase contribution only.

Maximum loadings of RSP, DOC, TP, Fe, Pb, Hg and OCS occurred in the lower St. Clair River, reflecting either additional sources or an artifact of sampling and/or loading calculations.

Effluent characterization data (MOE, 1987a) indicated that Dow Chemical and Polysar, located upstream of SR33.1 - SR34.98 on the eastern shore of the St. Clair River, were the most significant contributors of chlorinated organic loadings.

Relative to the 'head', loadings in the Detroit River 'mid' portion were elevated for RSP (6.5×10^6 kg/day), Cl^- (5.3×10^6 kg/day), TP (1.03×10^4 kg/day), Fe (1.6×10^5 kg/day), Pb (3.0×10^5 kg/day), Hg (4.6 kg/day), Zn (2.2×10^3 kg/day), HCB (0.1 kg/day), OCS (17 g/day) and total PCBs (3.9 kg/day). With the exception of HCB and OCS, these loadings are attributed to industrial and municipal inputs to the Rouge River and inputs to the Detroit River upstream of Fighting Island.

Non-point sources, although contributing minimally to flow rates, may have been partially responsible for the observed contaminant loading distributions. The Cole drain and Talford Creek (Figure 2) measured during 1984-85 as part of a Ministry of the Environment tributary study (MOE, 1987b) were identified as sources of HCB, QCB (pentachlorobenzene) and HCBD (hexachlorobutadiene) to the St. Clair River. Results of a joint Federal-Provincial St. Clair River Pollution Investigation report (DOE/MOE, 1986) also identified the Cole drain as a major contributor of HCB and OCS. Parts-per-million (ppm) levels were detected in sediments downstream of the Cole drain, while sediments upstream of this point contained only low parts-per-billion (ppb) levels.

Turkey Creek, Little River and Riviere aux Canards, which discharge to the Detroit River upstream of DT17.0E and DT9.3 - 5000, respectively (Figure 3), were identified by the MOE tributary survey to be sources of heavy metals and PCBs.

6.1.3 Changes in Loadings Between River Segments

The calculated loadings as well as relative loading differences expressed as percentage values are presented in Figure 9. This figure provides comparisons of relative increases/decreases in loadings between discrete segments of each river, enabling sources and depositional or loss areas to be distinguished.

Loadings derived from whole water concentrations (Table 6, Figure 9) revealed a number of trends. Both the St. Clair River 'mid' (SR33.1-SR34.98) and Detroit River 'mid' (DT17.4W, DT17.0E) were major sources of increased contaminant loadings. Loadings of Hg, HCB and OCS at Sarnia 'mid' increased 50, 360 and 230 times, respectively, over the St. Clair River upstream ('head') segment. These increases may appear magnified due to the relatively low levels of contaminants entering the St. Clair River from Lake Huron. Loading estimates for all other parameters increased 4 to 13 times in this interval. Octachlorostyrene loadings were observed to increase 161% from Sarnia to the lower St. Clair River, suggesting inputs of this compound immediately downstream of the 'mid' portion of the St. Clair River.

Loading reductions were observed for a number of compounds, both through Lake St. Clair and to a lesser extent, in the mid-to-lower portion of the Detroit River (Figure 9). Generally, reductions in Lake St. Clair were less pronounced, possibly due to re-suspension of particulates from wind-induced turbulence; fast throughput via the shipping channel; or as a result of additional sources to the lake. However, HCB and OCS loadings diminished to almost zero (95.5 - 95.0% decrease, respectively). Reductions in HCB and OCS levels may have occurred through a combination of accelerated losses to the atmosphere due to their low solubilities and relatively high vapour pressures which are typical of such compounds, and the absence of additional sources to the lake.

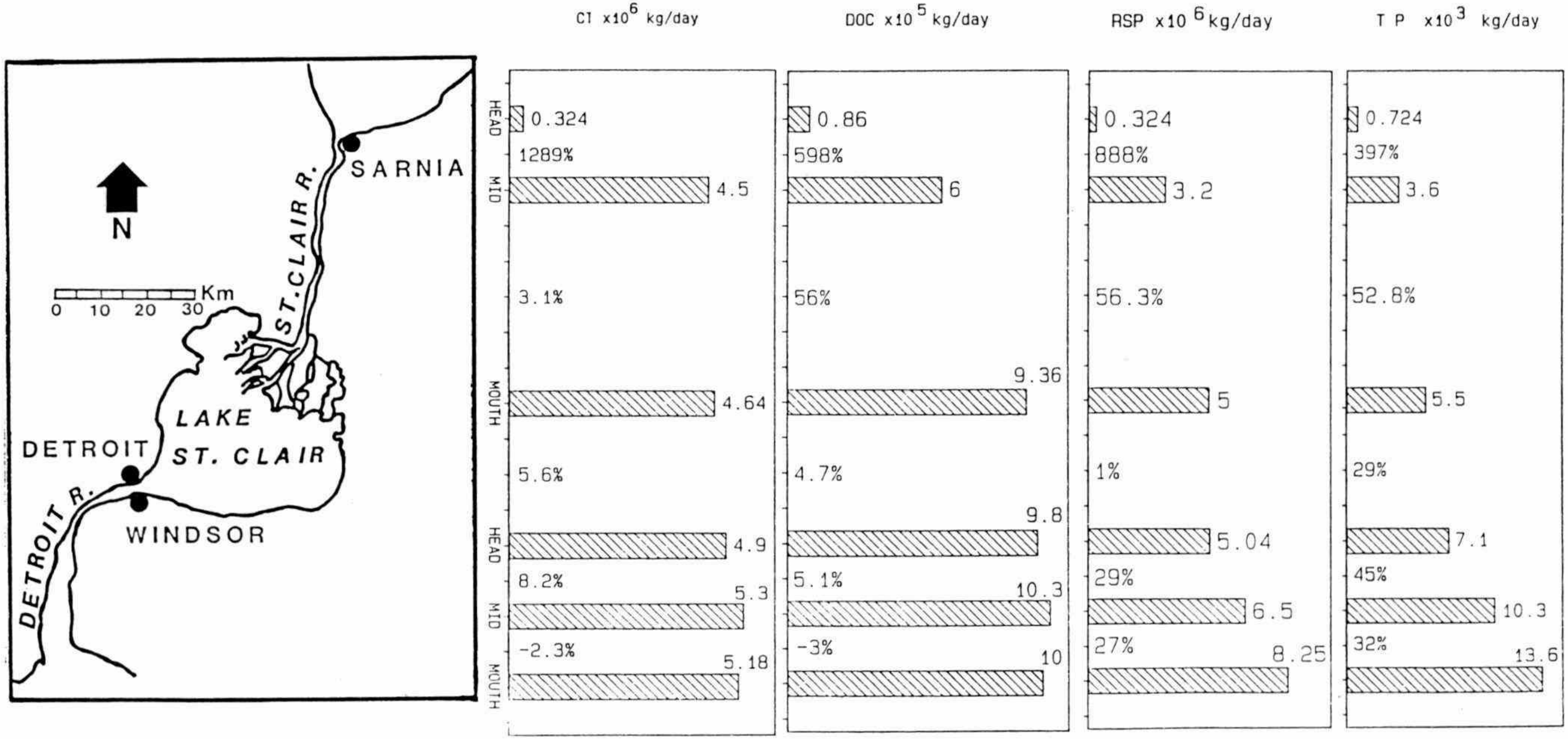


FIGURE 9: Relative loading differences between segments of the St. Clair and Detroit Rivers

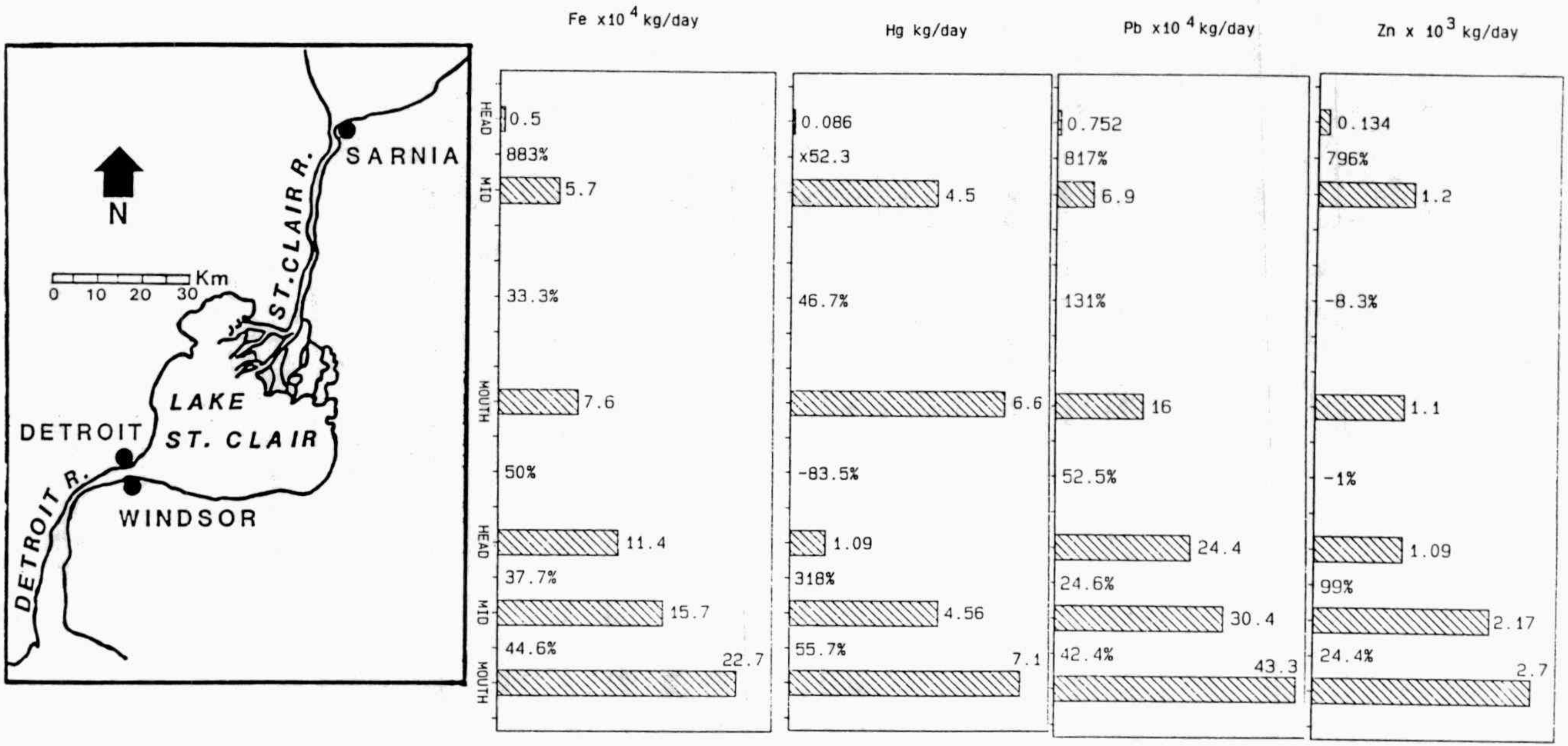


FIGURE 9: **con't.**

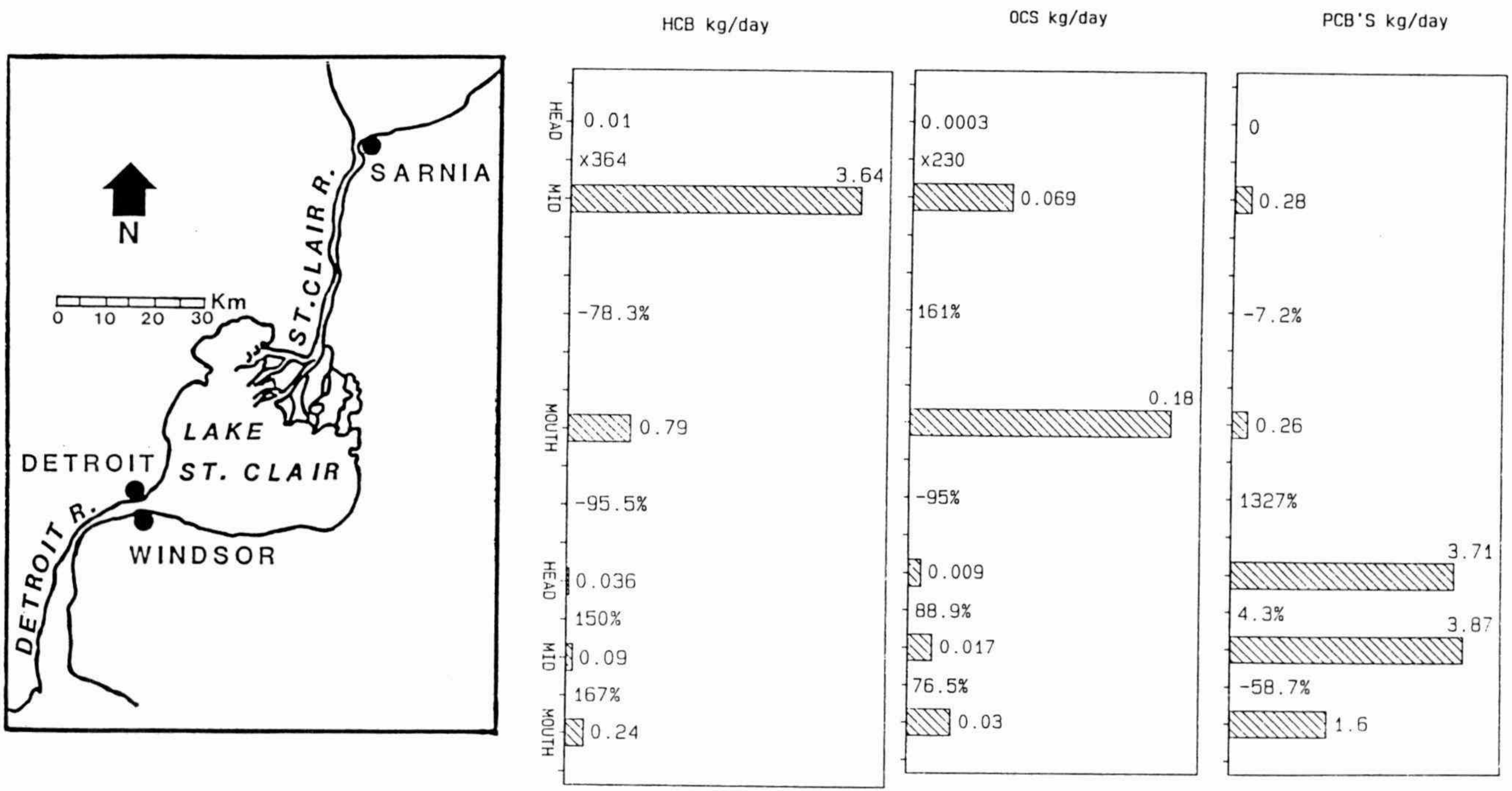


FIGURE 9: con't

Several factors may play a significant role in the observed reduction of a number of parameter loadings through Lake St. Clair. Low contaminant levels may have resulted from losses through various mechanisms. Volatilization in this high energy environment results in losses to the atmosphere, while hydrolysis, biolysis and photolysis act to break down organic compounds. Concentrations are further reduced as inputs of relatively clean tributaries tend to dilute overall lake concentrations. Results from the 1984-85 MOE investigation of tributaries entering Lake St. Clair (Sydenham, Thames, and Belle Rivers and Pike Creek) indicated non-detectable or trace levels of HCB, OCS and PCBs associated with whole water or particulates samples.

Settling-out of larger particles in the St. Clair River delta may have had the effect of increasing contaminant concentrations in particulates since smaller particles remained in suspension. Forstner and Wittman (1983) indicated that the increased surface areas of smaller particles allowed for a greater adsorptive capacity for contaminants, particularly metals. In this study, average lead, iron and zinc concentrations measured in suspended solids increased 24, 38 and 45% respectively from the St. Clair River mouth to the Detroit River head (Table 1), while suspended solid (RSP) levels in whole water increased by only 1% in the same interval (Table 2). Increases in loadings through Lake St. Clair were noted for DOC (4.7%), Cl^- (5.6%), TP (29%), Fe (50%), Pb (52.5%), RSP (1%) and PCBs (1327%). The increase in PCB levels may be attributed to nearshore inputs from western Lake St. Clair and municipal inputs to the Little River, located at the head of the Detroit River (Comba and Kaiser, 1985). These parameters may behave independently of loss mechanisms impacting most organic contaminants due to differences in physical/structural properties. Increases may be further attributed to inputs in this interval. An exception to this occurred for mercury as an 83% decrease in loadings was estimated to occur through Lake St. Clair. In this instance, settling-out of particulates and an absence of inputs may have more than offset particulate concentration increases through deposition of

coarse-grained material. Loadings for all parameters in the Detroit River increased without exception from the 'head' (DT30.8W; DT30.7E) to the 'mid' section (DT17.4W, DT17.0E) on the order of 4.3 to 318%. Surprisingly, increases of 90 to 150% were noted for loadings of OCS and HCB respectively; however, the magnitude of concentrations is not greatly elevated over background (St. Clair River 'head') concentrations. Although sharp increases were noted in relative values, absolute increases were quite marginal and likely fall within the bounds of field and laboratory error. ANOVA results indicated no significant differences between OCS and HCB concentrations on centrifuged particulates at the St. Clair River 'head' vs. Detroit River 'head' and 'mid'. Additional increases were noted from the mid to lower Detroit River for all parameters with the exception of DOC, Cl^- and PCBs. These increases were not as pronounced as observed in the head to mid range and may have been somewhat offset by reduced flow velocities in the lower river (U.S. COE, 1974), resulting in deposition of some coarser particulates in the intervening sections.

7.0 CONCLUSIONS

While the present data distinguished general contaminant loading trends spatially, more intensive surveys of greater duration will be necessary to fully describe the system under the variety of physical and chemical conditions which may occur.

The occurrence of intermittent elevated PCB levels in the upper Detroit River should be investigated to determine the source(s), frequency of occurrence and suggestions for remedial action.

While attempts have been made to minimize inaccuracies in estimating whole water concentrations from suspended solids, direct measurements through enhanced detection would greatly improve confidence in results.

Present methods for measuring organic contaminants in water must be refined to allow accurate quantification at ambient concentrations. Concentration of volumes of water larger than the conventional 1 litre samples obtained would probably have resulted in sufficiently low detection limits to obtain measurable values. For example, in the aqueous phase liquid extraction (A.P.L.E.) process, 200 litre whole water samples are centrifuged, yielding suspended solid and aqueous fractions. On-site solvent extraction of the resultant aqueous phase removes organic constituents which can be further concentrated in the laboratory.

This concentration of low-level organics from such a large sample volume enables compounds to be measured at a much more reliable level of detection. Review of the validity of this method for various applications has shown 80 to 90 percent recovery of spiked samples (Kuntz, 1984). Additionally, field validation of this method by Oliver and Nicol (1986) has provided favourable results.

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APPENDIX

APPENDICES

Estimation of contaminants in dissolved or aqueous phase from levels measured in suspended solids (Oliver, 1986):

$$K_{OC} = \frac{K_P}{F_{OC}} = \frac{C_S}{C_D F_{OC}}$$

K_{OC} = organic carbon corrected partition coefficient

K_P = partition coefficient (represents K_{OW})

F_{OC} = fraction organic carbon of solids

C_S = contaminant concentration on solids

C_D = contaminant concentration in dissolved phase

C_D can be estimated through re-arrangement of the above equation:

$$C_D = \frac{C_S}{K_{OC} F_{OC}}$$

log K_{OC} used in estimation:

HCB	6.1 ± 0.3
OCS	6.6 ± 0.3
PCBs	6.1 ± 0.3

TABLE A1: ANOVA SUMMARY - CENTRIFUGED PARTICULATES

Parameter	$F_{(CRUISE)}$	Sig. Level (α)	$F_{(STN)}$	Level of Sig.(α)
TOC	5.91	0.005	3.10	0.01
Solext	18.6	0.001	3.06	0.01
Fe	10.8	0.001	8.84	0.001
Pb	2.74	0.20	9.10	0.001
Hg	7.79	0.001	7.68	0.001
PCBs	2.30	N.S.	7.30	0.001
HCB	0.29	N.S.	2.80	0.02
OCS	0.52	N.S.	1.99	0.20
TP	3.91	0.05	3.41	0.005
Zn	0.10	N.S.	11.85	0.001

TABLE A1: ANOVA SUMMARY - CENTRIFUGED PARTICULATES (cont'd)

Parameter	No. Zones	Zone	Stations	Sig. Level (α)
TOC	2	1 2	2-13	0.01
	2	1 2	2-5, 9-13 1, 6-8	0.05
Solvent Extractables	2	1 2	1-7; 9-13 8	0.01
	2	1 2	2, 4-6, 9-13 1, 3, 7, 8	0.10
	3	1 2 3	2-5; 9-13 1, 3, 6, 7 8	0.20
Fe	2	1 2	1-5 6-13	0.01
	3	1 2 3	1-5 6-9; 11-13 10	0.05
Pb	3	1 2 3	1-3 4-7; 9, 11-13 8, 10	0.01
	4	1 2 3 4	1-3 4-7; 11-13 9, 10 8	0.05
	4	1 2 3 4	1-3 4-7, 9, 11-13 10 8	0.10
Hg	2	1 2	1-3; 6 4, 5, 7-13	0.05
	3	1 2 3	1-3; 6 4, 5, 7 8-13	0.10

TABLE A1: **ANOVA SUMMARY - CENTRIFUGED PARTICULATES (cont'd)**

Parameter	No. Zones	Zone	Stations	Sig. Level (α)
PCBs	2	1	1-5; 7, 9, 12	0.01
		2	6, 8, 10, 11, 13	
	3	1	1-5; 7, 9, 12	0.05
		2	6, 10, 11, 13	
		3	8	
	4	1	1-5, 7, 12	0.20
		2	9	
		3	6, 10, 11, 13	
		4	8	
HCB	2	1	1, 2, 4-13	0.05
		2	3	
	3	1	1	0.20
		2	2, 4, 6-12	
		3	3, 5, 13	
OCS	2	1	1-4; 6-13	0.01
		2	5	
		1	1, 2, 6-11, 13	0.20
		2	3, 4, 12	
		3	5	
TP	2	1	1-6, 9, 11-13	0.01
		2	7, 8, 10	
	3	1	2-5; 11-13	0.20
		2	1, 6, 7, 10	
		3	8	
Zn	3	1	1-5	0.01
		2	6, 7, 9, 11-13	
		3	8, 10	
	4	1	1-5	0.10
		2	6, 7; 11-13	
		3	9, 10	
		4	8	

Stn. Code:

Stn. #	Location	Stn. #	Location	Stn. #	Location
1	SR39-100	6	DT30.8W	11	DT9.3-2600
2	SR39-1500	7	DT30.7E	12	DT9.3-4000
3	SR10N	8	DT17.4W	13	DT9.3-5000
4	SR10S	9	DT17.0E		
5	CE17	10	DT8.7W		

TABLE A2: DUPLICATE RESULTS--CENTRIFUGED PARTICULATES
(% difference)

STN#	SURVEY	REPLICATE	DATE	TOT.ORG. CARBON mg/g	SOL.EXT. ug/g	IRON mg/g	LEAD ug/g	MERCURY ug/g	PCBs ng/g	HEXACHLORO-BENZENE ng/g	OCTACHLORO-STYRENE ng/g	TOT.PHOS. mg/g	ZINC ug/g
DT9.3-4000	1	1	3-May-84	37	3200	21	38	0.42	10	5	2	1.0	92
				(5.7)	(34.4)	(0)	(2.7)	(2.4)	(0)	(120)	(0)	(11.1)	(41.3)
DT9.3-4000	1	2	3-May-84	35	4300	21	37	0.41	10	11	2	0.9	130
DT17.4W	1	1	26-May-84	74	32366	28	200	0.49	955	0.5		2.5	520
				(6.8)	(11.9)	(0)	(5)	(22.4)	(13.1)	(0)		(4.2)	(2)
DT17.4W	1	2	26-May-84	79	36233	28	210	0.60	1080	0.5		2.4	510
DT17.4W	2	1	13-Jun-84		7500			0.30	425	8	2	1.7	
					(81.3)			(13.3)	(51.8)	(60)	(150)	(5.9)	
DT17.4W	2	2	13-Jun-84	71	13600			0.34	280	5	5	1.8	
DT17.0E	3	1	19-Aug-84	33	2720	26	53	0.62	10	6	0.5	1.1	140
				(3.0)	(88.6)	(4)	(69.8)	(3.3)	(200)	(16.7)	(0)	(9.1)	(0)
DT17.0E	3	2	19-Aug-84	34	5130	25	90	0.60	30	7	0.5	1.2	140
DT17.4W	3	1	20-Aug-84	30	12400	26	63	0.69	180	17	4	1.0	150
				(3.4)	(330.5)	(0)	(1.6)	(7.2)	(50)	(13.3)	(100)	(0)	(0)
DT17.4W	3	2	20-Aug-84	29	2880	26	62	0.74	120	15	2	1.0	150
DT17.0E	4	1	24-Nov-84	63	1493	31	45	0.29	10	14	3	1.1	150
				(4.8)	(23.9)	(0)	(2.3)	(7.4)	(150)	(7.7)	(0)	(0)	(0)
DT17.0E	4	2	24-Nov-84	66	1205	31	44	0.27	25	13	3	1.1	150
DT17.4W	4	1	24-Nov-84	78	8582	35	100	0.22	400	4	0.5	1.4	280
				(0)	(4.8)	(0)	(0)	(0)	(38.8)	(25)	(0)	(7.1)	(3.6)
DT17.4W	4	2	24-Nov-84	78	8187	35	100	0.22	555	5	0.5	1.5	290

TABLE A3: **ANOVA SUMMARY - WHOLE WATER**

Parameter	$F_{(CRUISE)}$	Sig. Level (α)	$F_{(STATION)}$	Sig. Level
RSP	4.29	0.02	2.0	0.20
DOC	2.04	N.S.	1.65	0.50
Cl^-	1.41	N.S.	13.23	0.001
TP	4.07	0.05	1.93	0.20
Fe	7.85	0.001	4.67	0.001
Zn	5.39	0.01	3.75	0.005

Parameter	No. Zones	Zone	Stations	Sig. Level (α)
RSP	1	1 2	1-13	0.05
	2	1 2	1-7; 9,12 8, 10, 11, 13	0.10
DOC	2	1 2	1-7; 9, 11-13 8, 10	0.10
Cl^-	3	1 2 3	1-3 4-7; 9; 11-13 8, 10	0.05
TP	2	1 2	1-4; 6, 9, 10 5, 7, 8, 11-13	0.05
	3	1 2 3	2, 3, 4 1; 5-7; 7-13 8	0.20
Fe	2	1 2	1-7; 9 8; 10-13	0.05
	3	1 2 3	1, 2, 4 3, 5-7; 9 8, 10-13	0.20
Zn	2	1 2	1-7; 9, 11-13 8, 10	0.01
	2	1 2	1-7; 9, 12-13 8; 10-11	0.05
	3	1 2 3	1-7; 12-13 9, 11, 8, 10	0.20

Station codes as per Table A1.

TABLE A4: DUPLICATE RESULTS--WHOLE WATER
(% difference)

STATION #	SURVEY	REPLICATE	DATE	SUSPENDED SOLIDS mg/l	DISS.ORG. CARBON mg/l	CHLORIDE mg/l	TOTAL PHOSPHORUS mg/l	IRON mg/l	ZINC mg/l
DT17.4W	1	1	26-May-84	11.10	1.90	12.31	0.0530	0.4800	0.0110
				(22)	(5.6)	(1.6)	(1.9)	(14.3)	(0)
DT17.4W	1	2	26-May-84	9.10	1.80	12.53	0.0520	0.4200	0.0110
DT17.4W	1	3	26-May-84	0.24	0.05	0.01	0.0005	0.2600	
DT9.3-4000	1	1	3-Jun-84	16.30	1.80	8.46	0.0190	0.3000	0.0030
				(2.5)	(0)	(2)	(46.2)	(73.3)	(567)
DT9.3-4000	1	2	3-Jun-84	15.90	1.80	8.63	0.0130	0.5200	0.0200
DT9.3-4000	1	3	3-Jun-84	0.50	0.20	0.13	0.0110	0.0090	0.0005
DT17.0E	2	1	12-Jun-84	8.30	1.70	8.02	0.0210	0.1300	0.0020
				(4.8)	(0)	(0.9)	(200)	(23.1)	(0)
DT17.0E	2	2	12-Jun-84	8.70	1.70	8.09	0.0070	0.1600	0.0020
DT17.0E	2	3	12-Jun-84	0.05	0.40	0.01	0.0030	0.0030	0.0005
DT17.4W	2	2	13-Jun-84	5.60	2.20	11.25	0.0190	0.2000	0.0040
				(7.1)	(4.8)	(0.01)	(15.8)	(11.1)	(33.3)
DT17.4W	2	1	13-Jun-84	6.00	2.10	11.24	0.0220	0.1800	0.0030
DT17.4W	2	3	13-Jun-84	0.17	0.10	0.01	0.0060	0.0005	0.0005
DT17.0E	3	1	19-Aug-84	12.20	1.80	9.75		0.2400	0.0020
				(4.3)	(5.6)	(3.9)		(8.3)	(50)
DT17.0E	3	2	19-Aug-84	11.70	1.90	9.38		0.2600	0.0030

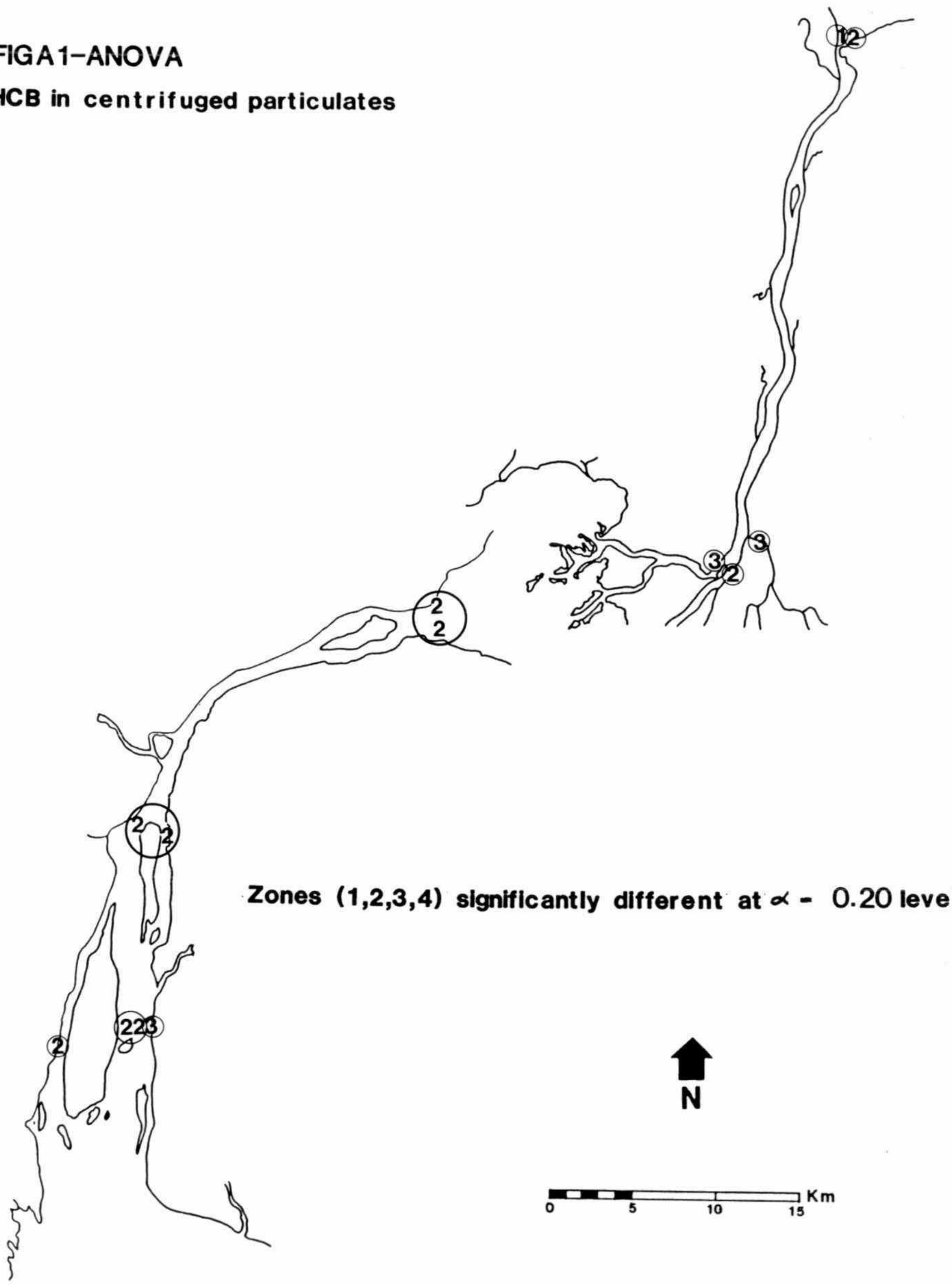
Table A4: (cont'd)

STATION #	SURVEY	REPLICATE	DATE	SUSPENDED SOLIDS mg/l		DISS.ORG. CARBON mg/l		CHLORIDE mg/l		TOTAL PHOSPHORUS mg/l		IRON mg/l		ZINC mg/l	
DT17.0E	3	3	19-Aug-84	0.02		0.05		0.14				0.0010		0.0005	
DT17.4W	3	1	20-Aug-84	36.40		2.10		9.98				0.7600		0.0070	
					(0.8)		(5)		(1.7)				(2.7)		(0)
DT17.4W	3	2	20-Aug-84	34.10		2.00		10.16				0.7400		0.0070	
DT17.4W	3	3	20-Aug-84	0.41		0.05		0.21				0.0010		0.0005	
DT17.0E	4	1	23-Nov-84	7.40		2.10		10.93		0.0250		0.4900		0.0040	
					(175.7)		(5)		(0.9)		(4.2)		(12.2)		(0)
DT17.0E	4	2	23-Nov-84	20.40		2.00		10.83		0.0240		0.5500		0.0040	
DT17.0E	4	3	23-Nov-84	0.71		0.05		0.05		0.0015		0.0150		0.0030	
DT17.4W	4	1	24-Nov-84	22.30		1.90		11.70		0.0340		0.4200		0.0060	
					(3.4)		(0)		(1.9)		(21.4)		(7.1)		(100)
DT17.4W	4	2	24-Nov-84	23.10		1.90		11.92		0.0280		0.4500		0.0120	
DT17.4W	4	3	24-Nov-84	1.52		0.05		0.01		0.0005		0.0015		0.0020	

REPLICATE CODE:
- 1: Grab sample
- 2: Replicate
- 3: Blank

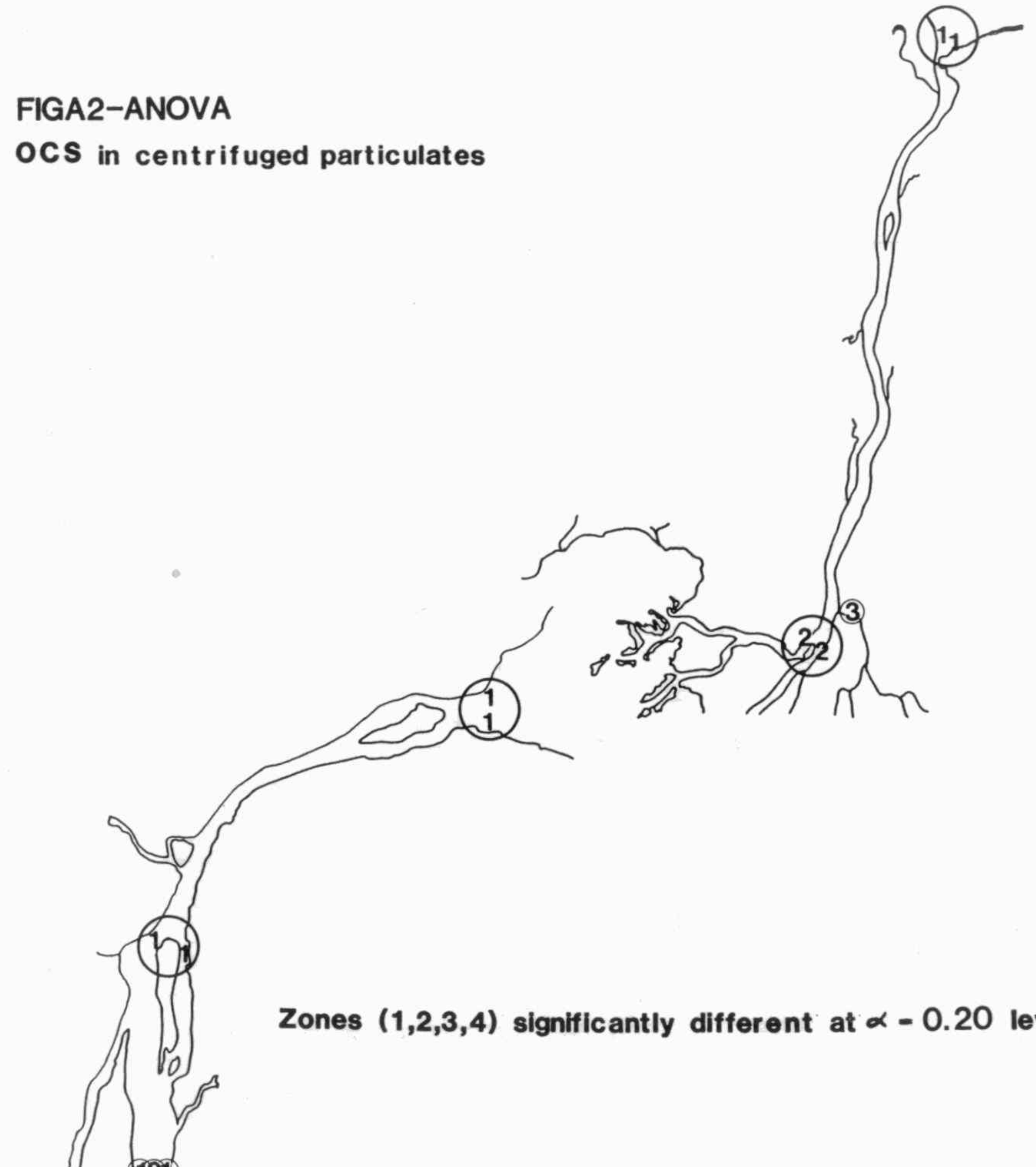
FIGA1-ANOVA

HCB in centrifuged particulates



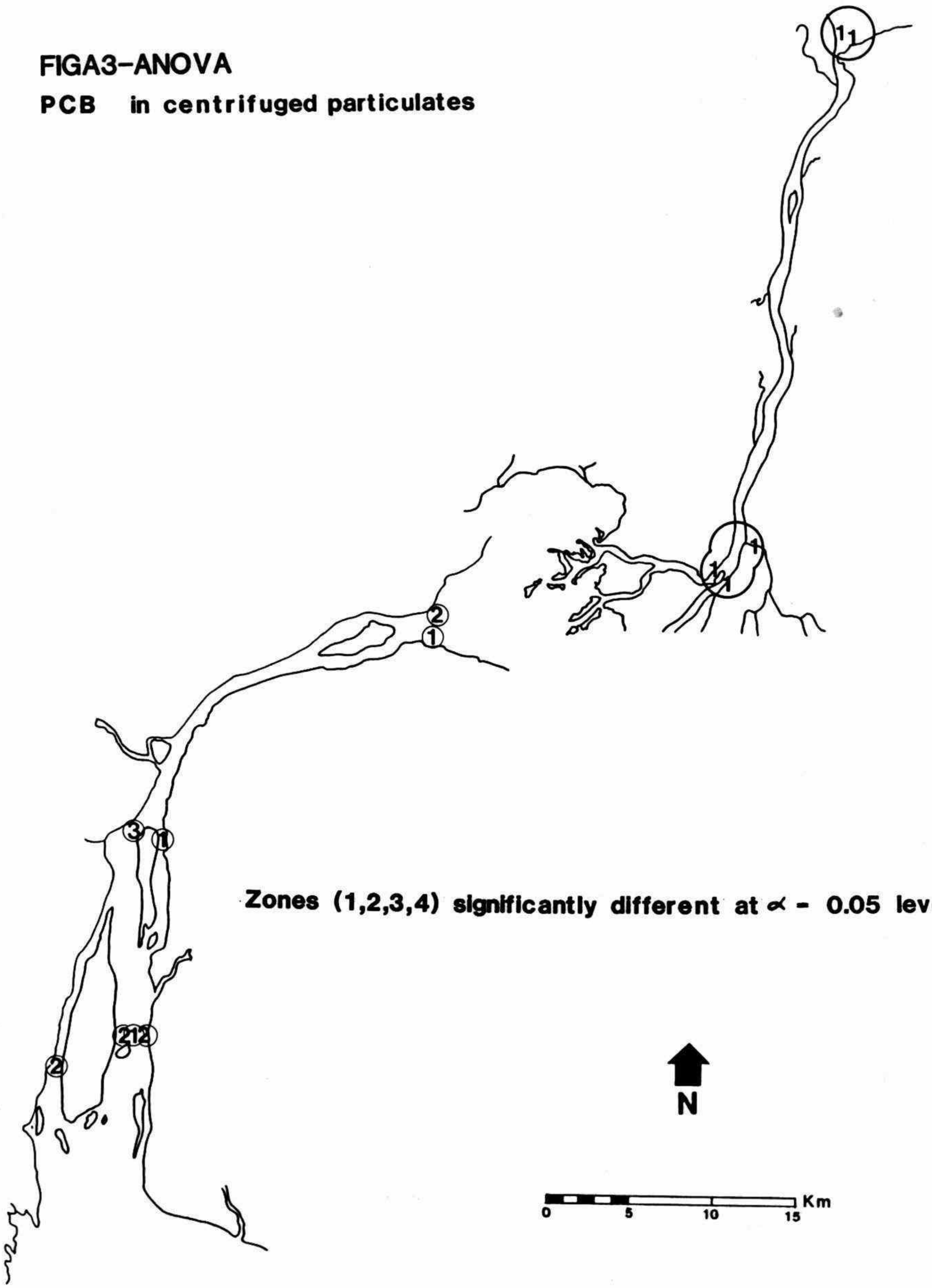
FIGA2-ANOVA

OCS in centrifuged particulates



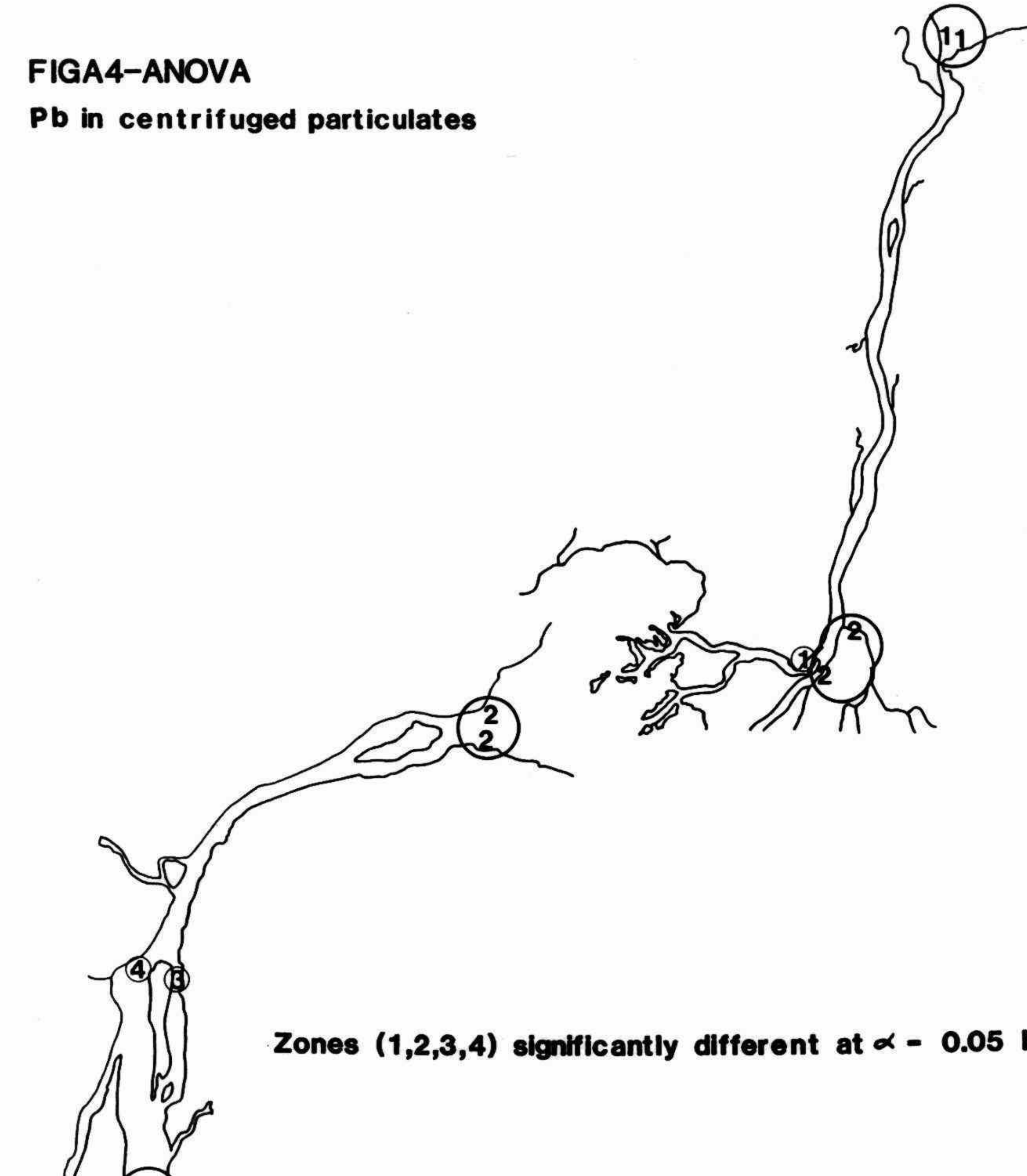
FIGA3-ANOVA

PCB in centrifuged particulates



FIGA4-ANOVA

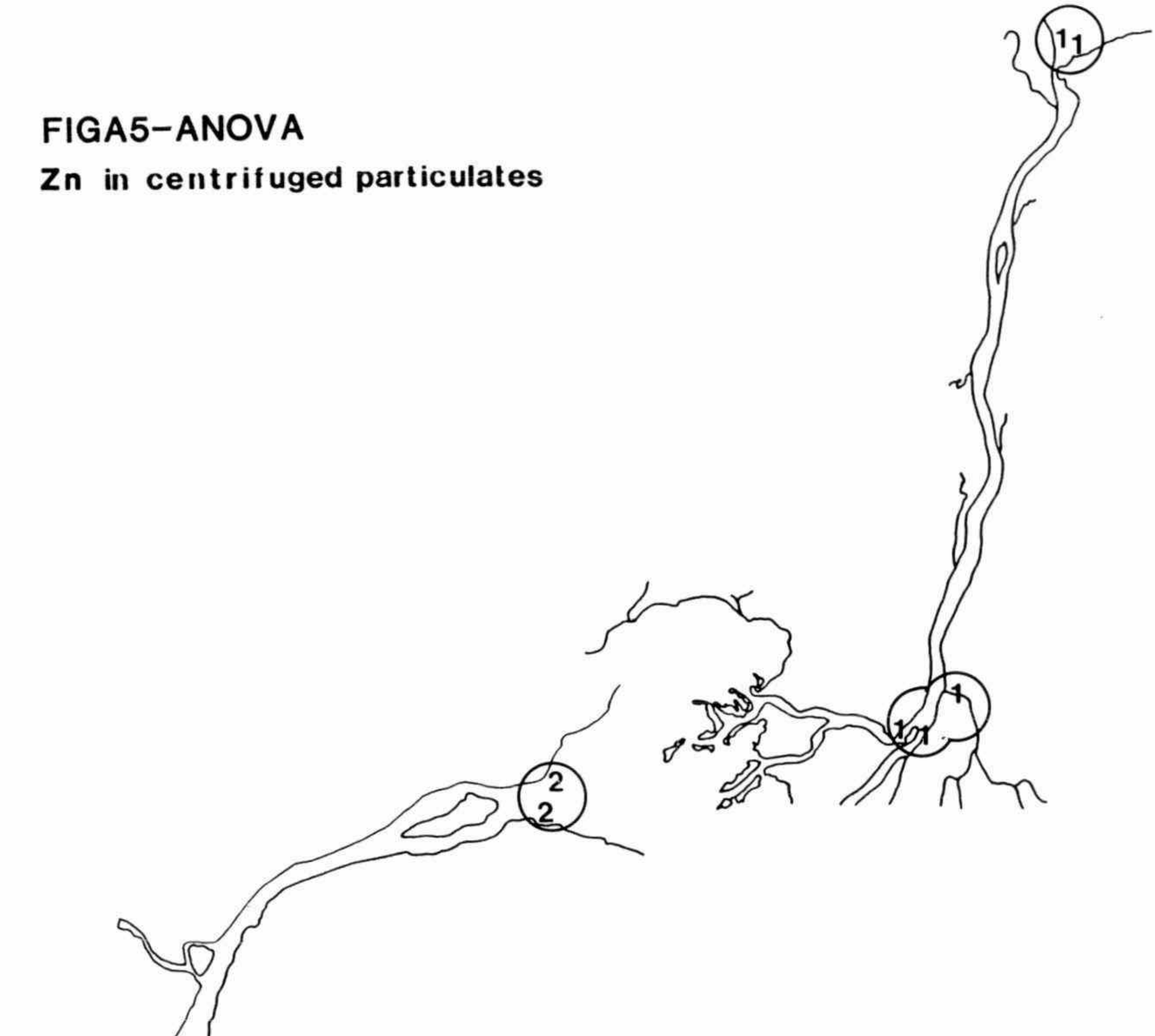
Pb in centrifuged particulates



Zones (1,2,3,4) significantly different at α - 0.05 level

FIGA5-ANOVA

Zn in centrifuged particulates



Zones (1,2,3,4) significantly different at α - 0.10 level